STUDIES ON THE ADSORPTION AND DESORPTION BEHAVIOUR OF TRACE METALS IN SOILS

By

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In the Name of 'ALLAH' "Most Gracious, Most Merciful"

"Proclaim ! And thy Lord is most Bountiful"

"He Who taught (the use of) the Pen,"

"Taught man that which he knew not."

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Summary

Chapter 1 gives a general introduction to trace elements in soils. A brief discussion about their occurrence, forms in soils and state in which plants utilize them has been made. Physiological role and deficiency symptoms due to short supply have been identified. Much emphasis has been given to the adsorption and desorption behaviour and factors affecting adsorption and desorption of trace metals. Zinc, Copper and Nickel have been the focus of the Chapter.

Chapter 2 lays emphasis on the methods and materials used for conducting the different experiments. Moreover a brief history and some physical and chemical properties of the five British soils have been mentioned in this chapter.

Chapter 3 elucidates the development of different procedures for adsorption and desorption of zinc in soils. After a series of experiments an 18 hour shaking time for adsorption and desorption of zinc in soils was selected. The results obtained from these experiments suggest that prolonging the time of zinc contact with soils increases the adsorption of zinc, however it is more significant with lower concentrations than higher concentrations. Furthermore the soils high in clay content adsorbed more zinc compared to coarse soils. It is comparatively easier to desorb zinc from a soil at higher metal concentration than low concentration. Generally dilution by deionized water did not desorb a significant amount of adsorbed

metal perhaps due to the inability of deionized water to break the strong bonds between metal and soil components

Chapter 4 investigates adsorption and desorption behaviour of zinc, copper and nickel in 0.1M $NaNO_3$ background electrolyte. The results suggest that due to reducing the background interferences by using an electrolyte, lesser amount of zinc was adsorbed compared to deionized water used in chapter3. Moreover it shows that zinc and nickel have almost similar behaviour towards adsorption in soils. Behaviour of copper indicates high affinity of adsorption by soils and is completely different from zinc and nickel. Clayey soil adsorbed higher amounts of metals than other soils. Although texture appeared to be dominant, other properties of soils in respect of adsorption behaviour could not be neglected, especially pH and organic matter. All the adsorption data regarding these metals fit well to both Langmuir and Freundlich equations. The desorption data suggest that copper formed strong bonds with soil components, perhaps with clay, and therefore very low percent of copper was desorbed with dilution by electrolyte. The other two metals were recovered up to 50% except in the clayey soil. Langmuir equation better fitted the desorption data of all metals compared to Freundlich equation.

Chapter 5 illustrates that temperature has an effect on adsorption and desorption of zinc in soils. Adsorption of zinc increases with the increase of temperature and generally desorption decreases. However the desorption of zinc at higher temperatures sometimes showed no

significant decrease in some soils. It suggests that higher temperature weakened the binding constants of zinc with those soils. The results also show the effect of dilution on the desorption of zinc at four different temperatures and suggest that activation energy increased with increased dilution. This is because to break the existing bonds of zinc with soil. It is necessary for desorption reactions to have a significant activation energy, while it is not necessary for adsorption reactions to have a significant activation energy. The low activation energy of all soils suggests that diffusion have played a major role in all reactions.

Chapter 1

Trace metals in soils

1.1 Introduction

Microelements, trace elements and minor elements are the synonymous terms referring to the elements whose total concentration in the soil is normally less than 1,000 mg kg^{-1}. Soil chemists have long recognized that knowledge of the elemental composition of soils is generally of little use in assessing the availability of these elements to plants. For example the common occurrence of Fe and Mn deficiency in plants despite the relatively high concentrations of Fe and Mn in many soils. Therefore chemical soil tests have relied on measurement of extractable or labile fractions of elements. Such tests are empirical and provide little basis to relate metal extractability to the chemical forms of the metal in the soil.

Soil microelements fall into two categories, the essential micronutrients like Zn, Cu, Mn, and Mo, which are required by plants at normal concentration (ranging from 0.1mg Kg^{-1} for Mo,to 100mg Kg^{-1} for Mn; White, 1987). At higher concentrations they may become toxic. The other category has no beneficial role (e.g. Pb, Cr, Cd, and Ni) and are toxic in soil at levels greater than a few mg Kg^{-1}. A large number of elements are required for growth and reproduction of plants and animals. Of these nutrients only a few are needed in large amounts for agricultural production. Deficiencies of those remaining elements,

which are required in lesser amounts are most frequently related to specialized crops or certain types of soil. As the demand for higher yield increases and the plant's requirement for major elements is more efficiently met, other nutrients are more likely to become limiting. To obtain the higher yield and good quality of crops to meet human requirements, attention should be given to higher yielding plant varieties, and use of N.P.K fertilizers along with regular supply of micronutrients to soil. The decreasing availability of farmyard manure (rich in trace metals), improper crop rotation and intensive cultivation have increased the need for micronutrients in terms of their availability to plants. Therefore better understanding of the chemistry and behaviour of these nutrients is very important, otherwise the deficiency problems may become very serious in terms of drastic low production of crops to fulfil human requirements.

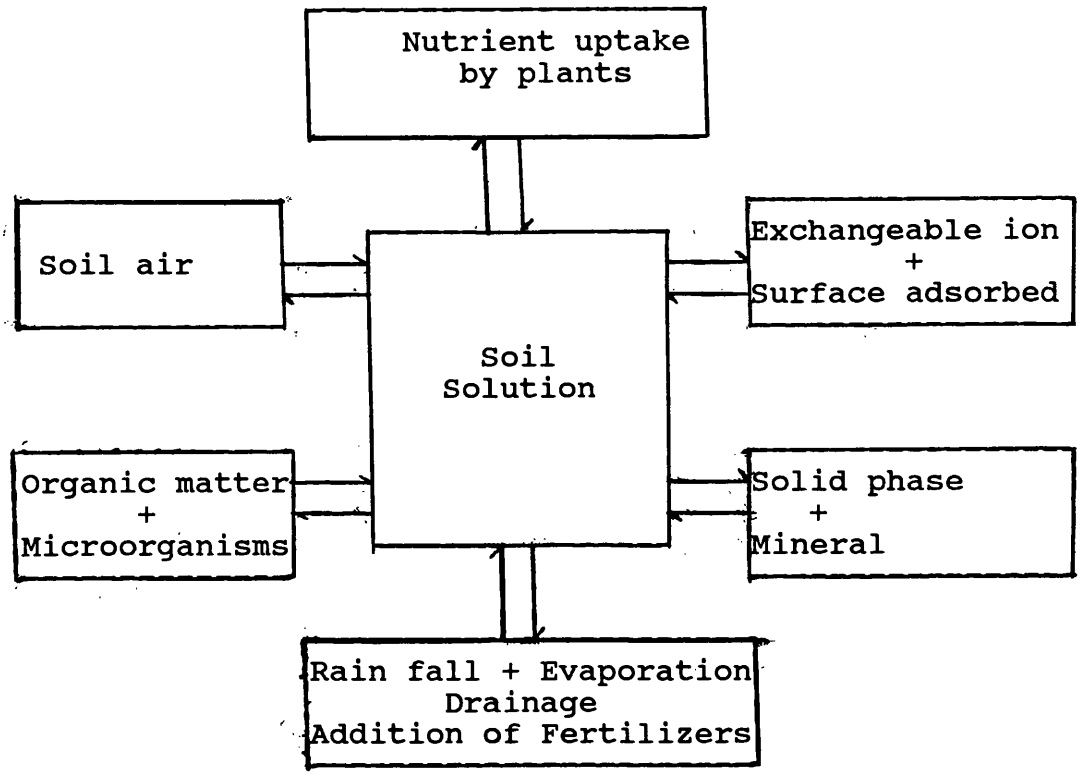
Table 1.1. Total contents of trace metal ions in the lithosphere and in soils

Element	Average in lithosphere ($mg\ Kg^{-1}$)	Soil content ($mg\ Kg^{-1}$)
Iron	50,000	10,000 - 300,000
Manganese	1,000	2,000 - 3,000
Nickel	100	10 - 1,000
Chromium	100	5 - 3,000
Zinc	80	10 - 300
Copper	70	2 - 100
Cobalt	40	1 - 50
Lead	10	2 - 200
Molybdenum	2	0.2 - 5
Cadmium	0.2	0.01 - 7

From: Bohn, Mc Neal and O' Connor, 1985 p 311

Trace metal distribution in terms of amounts of micronutrients in rocks and soils has been well described by Hodgson (1963), Phipps (1981), and Bohn et al. (1985). Table 1.1 indicates the total contents of trace metal ions in the lithosphere and in soils.

McLaren and Crawford (1973 a,b) observed that trace elements usually occur in soils in six different fractions; (a) in the solution as ionic or complexed forms, (b) on normal exchange sites, (c) adsorbed on specific sorption sites, and not removed by reagents which are normally used for determining the exchangeable ions, (d) occluded in soil oxide materials, (e) associated in biological residues and living organisms, (f) held in the lattice structure of primary and secondary minerals. The equilibria and reactions between these forms are fundamental to an understanding of the soil chemistry of trace metals. The dynamic equilibria according to Lindsay (1979) occur in soils as such



Flg: 1.1 The dynamic equilibria that occurs in soil From Lindsay (1979).

Zinc and copper occupy important position among the elements essential for plants and animals, are absorbed as Zn(II) and Cu(II) respectively and are translocated to the roots as the free ions, however copper ions are predominantly translocated to the shoots in anionic form. Zinc concentration in plant dry matter is at least three- or four-fold greater than copper. Both the metals are known to be essential constituents of many plant enzymes. For example carbonic anhydrase, alcohol dehydrogenase and superoxide dismutase (Vallee et al; 1976), for zinc and some other studies on zinc deficient plants suggest that it is specially required for many other plant enzymes including additional dehydrogenases, DNA and RNA nucleotidyltransferases (polymerases) and some peptidases

and protinases. Copper is important and essential constituent of a series of enzymes known as oxidase in which molecular oxygen is used directly in the oxidation of substrate, these comprise cytochrome oxidase, phenol oxidase, laccase, ascorbic acid oxidase and amino oxidase. It is believed that catalytic activity of these enzymes depend on ability of their copper to undergo reversible change in oxidation state between Cu(II) and Cu(I). In addition to the oxidases, plants have superoxide dismutase, an enzyme containing both copper and zinc which plays a vital, protective role in plant metabolism. Copper also plays a role in photosynthesis as an essential constituent of plastocyanine. This enzyme is located in chloroplasts and forms part of the electron transport chain between the two photochemical systems of photosynthesis. The precise role of copper in plastocyanine is not known, but it has been assumed to a reversible change in oxidation state.

Nickel is claimed to be essential and is absorbed in the ionic form as Ni^{2+} from the soil or culture media. It is required as a component of the urease enzyme, at least in some species (Eskew et al; 1983). It is also required by animals as an essential nutrient (Underwood, 1977). Though nickel is not yet accepted as an essential element for plants, it has been shown when soyabeans were deprived of nickel, urea accumulated in toxic concentrations in the leaf tip (Eskew et al; 1983). This occured regardless of whether the plants were supplied with inorganic nitrogen or were dependent on dinitrogen fixation. Nickel, like

cobalt, substitutes for iron in ferromagnesian minerals. It is not known to what extent nickel is incorporated into clay minerals in normal soils but it is concentrated in hydrous oxides of iron and manganese (LeRiche and Weir, 1963). The main concern with this element is the occasional report of its toxicity in some plants growing on soils developed from ultrabasic rocks. In studies based on serpentine soils in Aberdeenshire and on sand culture it has been shown that oats are particularly sensitive to nickel toxicity (Hewitt, 1983). Liming alleviates nickel toxicity, an effect partly due to raising pH but largely due to increasing the supply of calcium (Halstead, 1968).

The physiological role of these metals is wide and the deficiency symptoms in different plants and trees are very prominent. For example, the characteristic symptom of zinc deficiency is a failure of leaves to expand and stems to elongate, giving a terminal rosette effect. Fruit trees, particularly citrus are frequently affected by zinc deficiency and maize, tomato and cotton are especially sensitive. In fruit trees such as citrus, apple and peach, the mature leaves may show the first symptoms as pale green to yellow interveinal mottling, while more severe effects on growth and rosetting occur in the terminal leaflets of young shoots. The older leaves of maize may have purple tints while yellow or white interveinal chlorotic stripes develop in the younger leaves. In tomato and cotton the symptoms appear as irregular areas of interveinal chlorosis which become necrotic. Lindsay (1972b) reviewed the pattern of zinc deficiency and

indicated the interveinal chlorosis the first sign of zinc deficiency in crops like maize.

Crops vary in their response to low supplies of copper. Cereals and fruit trees can be seriously affected with substantial losses in the yield, while, for example, sugarbeet shows few visible symptoms and yield losses are only small. In cereal crops the symptoms of deficiency appear during tillering when the leaves become twisted or rolled and their tips turn grey or white; ear emergence and grain filling are seriously affected. In some fruit trees the leaves of terminal shoots become dark green and curled and may then develop brown or necrotic areas. This is usually followed by withering of the leaves, defoliation and death, or die back of the shoot.

Nickel toxicity and environmental effects are very wide but its deficiency symptoms in plants are uncommon. However it has been shown that soyabeans develop necrotic lesions in the leaf tip when it was not supplied nickel (Eskew et al; 1983). Nickel has also been observed to stimulate seed germination and growth of a number of plant species, such as potatoes and grapes (Hutchinson, 1981).

As modern agronomic practices have led to wide occurence of zinc and copper deficiencies in plants, the use of zinc and copper fertilizers to correct the deficiencies has become more common. The development and wide spread use of atomic absorption spectrophotometry as a suitable instrument of measuring trace metals has resulted in considerable interest and research into the chemistry of these elements in soils. Soil tests to assess

available zinc and copper in soils are now common. Although in the past much emphasis has been placed on deficiencies, possible zinc and nickel toxicity problems are becoming of increasing concern. This is due to activities such as land disposal of high metal content sewage sludges.

1.2 Chemistry and behaviour of trace metals in soils

1.2.1 Metals in soil solution

The trace elements in solution may be either leached from the soil or reprecipitated as a hydroxide, carbonate, sulphate, phosphate etc; or incorporated into a pedogenic silicate. Less specifically, it may be adsorbed on to charged surfaces of clay particles or organic matter. Identification of the particular inorganic precipitated forms in which trace elements are present has been attempted through the prediction of phase equilibria, as summarized by Lindsay (1972a). Lindsay (1979) in an another study described the soil solution, as the 'liquid phase' that envelops the solid phase, while Russell (1973) defined soil solution as the water in soil containing soluble salts. Soil Science Society of America (1965) defined soil solution as 'the aqueous liquid phase of the soil and its solutes consisting of ions dissociated from the surfaces of soil particles and of other soluble materials'. There are three possible sources from which plants can extract nutrients; the soil solution, the exchangeable ions, and the readily decomposable minerals;

and it is very difficult to separate out the relative importance of these sources for any particular plant. The inter-relation of sources may be written:

$$\text{M (unavailable)} \xrightarrow{k1} \text{(intermediate availability)} \xrightarrow{k2}$$
$$\text{(exchangeable)} \xrightarrow{k3} \text{(solution)}$$

where M represents a nutrient and k1, k2 and k3 are rate constants associated with each step towards the right; $k1 \ll k2 \ll k3$ and appreciable change occurs in months, weeks and minutes, respectively. Thus if the soil is in equilibrium with the exchangeable cations and adsorbed anions, and if any nutrient (except nitrate whose supply is principally from mineralized organic matter) is removed from the solution, at least a part of this loss will be made good from the nutrient reserves of the solids. Solid materials of the soil keep the soil well buffered both for pH and for all nutrients except nitrate.

Soil solution acts as a transport medium bringing the trace metals into contact with root surfaces where they may be absorbed. The plant roots absorb nutrients from the soil solution through the processes of convection or diffusion and thus the concentration of nutrients in the soil solution is a factor determining their rate of uptake by roots. Over long periods as, for example, a growing season, the release of nutrients from the more readily decomposable minerals (sources of intermediate availability) in the soil will also be important in sustaining the concentration in solution and the rate of uptake by roots.

The liquid phase is one of the four component multiple-phase systems which the soil comprises. However it contains only a very small fraction of trace metals Jenkins and Wyn Jones (1980) quoted the ranges of some micronutrient metal concentrations and their degree of complexing in soil solution, which are given in Table 1.2.

Table 1.2. Concentration and degree of complexing of some micronutrients in solution.

Element	Total element in soil solution (μM)	degree of complexing (%)	(Mean)
Cobalt	0.007 -0.2	8-50	25%
Zinc	0.03- 3	28-99	50%
Manganese	0.02-68	84-99	90%
Copper	0.01- 0.6	89-99.9	>90%

After Jenkins and Wyn Jones, 1980 p13

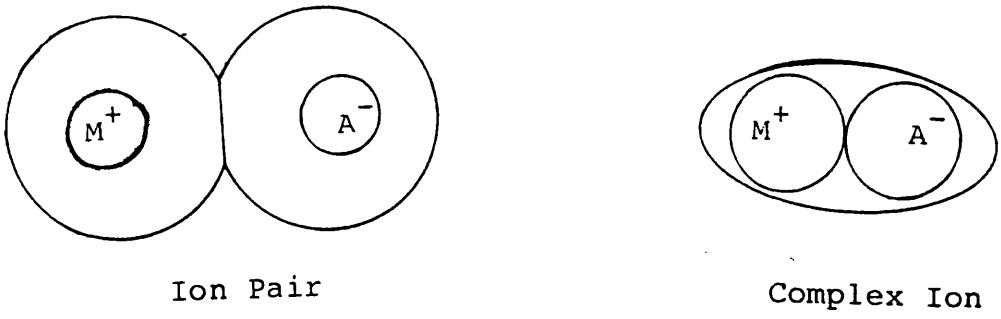
According to Loneragan (1975) the dominant inorganic ions of Co, Cu, Mn and Zn in solution occur as divalent cations M^{2+} while Fe^{3+} may also exist in very acid soils. In neutral and alkaline soils the monovalent hydroxy cations $M(OH)^{+}$ would also be important. Much less is known of the concentration and forms of Fe and Mo in soil solutions. Most recently Brady (1990) has summarized the forms of eight micronutrients dominant in soil solution and are given in Table 1.3.

Table 1.3 Forms of micronutrients dominant in soil solution

Micronutrient	Dominant soil solution forms
Iron	Fe^{2+}, $Fe(OH)_2^{+}$, $Fe(OH)^{2+}$, Fe^{3+}
Manganese	Mn^{2+}
Zinc	Zn^{2+}, $Zn(OH)^{+}$
Copper	Cu^{2+}, $Cu(OH)^{+}$
Molybdenum	MoO_4^{2-}, $HMoO_4^{-}$
Boron	H_3BO_3, $H_2BO_3^{-}$
Cobalt	Co^{2+}
Chlorine	Cl^{-}

From data in Lindsay (1972)

Many transition metals are present as complex ions or ion pairs. When ions and molecules interact they can bond together and form complex ions or ion pairs after losing their separate identities, (Bohn et al; 1985). Complex ions are usually defined as the combination of a central cation with one or more ligand. A ligand is defined as any ion or molecule in the coordination sphere of the central ion, such as H_2O in the case of $Fe(H_2O)_6^{3+}$ (hexaquoiron (III) complex ion). As hydrated ions are linked electrostatically and behave like a single unit, the ion pairs are thought to form by ligand attachment outside the inner solvation sphere similarly. This is shown diagrammatically in Figure 1.2.



Ion Pair

Complex Ion

Figure 1.2 Diagram of an ion pair and complex ion. From Bohn et al. (1985) p 35.

The concentration of zinc in soil solution plus exchangeable Zn is about 0.26% of the total amount of zinc in soil as reported by Mandal and Mandal (1986) in lowland rice field soils. In acid soils zinc occurs in solution mainly as Zn^{2+}. For example in three acid soils (pH 4.8-5.7), 71-76 percent of the zinc in solution was estimated by Riley and Barber (1971) to be present as Zn^{2+}. At higher pH values $Zn(OH)^{+}$, $Zn(HCO_3)^{+}$ and $ZnCO_3^{0}$ are present in concentrations which depend on the pH and partial pressure of carbon dioxide. In four contaminated soils about 39 percent of the total zinc was associated with iron and manganese oxides and about 28 percent with the carbonate fraction but less than 10 percent was organically bound (Hickey and Kittrick, 1984). Some work has been done at comparatively high rates of addition where $Zn(OH)_2$ and, in calcareous soils, $ZnCO_3$ can be precipitated. In the presence of $NH_4H_2PO_4$, zinc phosphate has been identified (Kalbasi et al; 1978). More usually the concentration of zinc in the soil solution is controlled, at least in dilute solution, by adsorption/desorption reactions. The solubility of soil

zinc decreases as the pH increases. Jeffery and Uren (1983) in one study concluded that the total concentration of zinc in the soil solution decreased about 100-fold as the pH of the soil increased from 4.4 to 7.5. In another study, Sims and Patrick (1978) investigated the effects of pH and redox potential and showed that greater amounts of zinc were extracted (by sodium acetate and potassium pyrophosphate) at low Eh and pH than at high Eh and pH, and complexation by organic matter was greater in the soil of low Eh. Shuman (1980) reported that the zinc held by ion exchange is in dynamic equilibrium with Zn^{2+} in soil solution or organically complexed zinc.

Copper occurs in soils as Cu(II). At pH values of about 7 and above, $Cu(OH)^{+}$ is present in significant concentrations and may enter into soil adsorption reactions. Lindsay (1979), suggested that the solubility of soil copper is controlled by that of cupric ferrite and that the equilibrium for copper can be represented by the equation

$$\log Cu^{2+} = 2.8 + 2\ pH$$

but it seems more likely that most soil copper exists chemisorbed by or occluded in hydrous oxides of iron, aluminium or manganese and complexed with organic matter.

In peats of pH 3.5, 60-90 percent of the copper in aqueous extracts was found to be organically complexed, and the raising the pH to 6.0 increased the degree of complexation to >98 percent (Hodgson et al; 1965). These complexes are very stable and Schnitzer (1969) has reported that of nine divalent ions , copper formed the

most stable complex with fulvic acid, involving carboxy and phenolic groups. Complexation of copper by organic matter may control its availability. Another study by McLaren et al. (1981) on the adsorption of copper by soil materials at low equilibrium solution concentrations demonstrated that iron and manganese oxides and humic acid adsorbed the greatest amounts, and that within the range of normal agricultural soils pH had little effect on the solution concentration of copper.

1.2.2 Metals on exchange sites

The permanent charge sites of layer silicate clays retain metal cations by non-specific electrostatic forces and, in the absence of conditions that would favour metal hydrolysis (e.g. high pH), divalent (M^{2+}) and trivalent (M^{3+}) transition and heavy metal cations show typical ion exchange behaviour on layer silicates (el-Sayed et al; 1970, McBride, 1976; McBride, 1980c). Both ultraviolet (UV)-visible and electron spin resonance (ESR) spectroscopy have confirmed that ions such as Cu^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} retain their inner hydration sphere as well as a high degree of rotational mobility on smectite exchange sites, offering direct support for the involvement of electrostatic forces only (Clementz et al. 1973; McBride, 1979b; Schoonhedt, 1982). Thus strength of metal bonding should depend only on the charge and hydration properties of the cation.

Cations released by weathering and organic decay vary greatly in ion charge and size, and they respond

differently to the ions and surfaces encountered in the soil, some tend to remain in solution but to be associated with the surface of charged solid phases and are known as the exchangeable ions, while some which are poor competitors for surface charge remain in bulk soil solution (soluble ions). The exchangeable ions are defined as those released from soil by solutions of neutral salts. The sites from which cations can be released by the cation from a neutral salt solution are called exchange sites. The exchange sites can regulate the metal concentration in soil solution by their release of cations. Also, the metal ions they adsorb are readily exchangeable, so they can be taken up by the plants. The fraction of soil metals adsorbed on these sites varies and depends on the cation exchange capacity of a soil.

Soon and Bates (1982) reported that a low pH value increased the proportion of trace metals (Cd, Ni, Zn) in the exchangeable form in soil. Sims and Patrick (1978) reported that amounts of manganese and iron held on exchange sites were affected by pH and redox potential. Their results showed that at low pH and Eh more manganese and iron can exist on exchange sites.

1.2.3 Metals on specific sorption sites

The specific sorption sites on soils are various soil constituent surfaces which adsorb cations that can not be removed by reagents normally used for determining the exchangeable cations (McLaren and Crawford, 1973b). Much evidence is found in the literature concerned with

adsorption and desorption of metals that transition and heavy metals in soil, when present at trace levels, are largely retained in non-exchangeable forms.The extraction of such metals requires extreme treatments, including the oxidative degradation of organic matter and dissolution of Fe and Mn oxides (Shuman, 1979).

It is now established that metal oxides and hydroxides as well as aluminosilicates provide surface sites for chemisorption of heavy metals. Indirect evidence for the formation of surface-metal bonds includes:

1. The release of as many as two H^+ ions for each M^{2+} ion adsorbed (Forbes et al; 1976).
2. The high degree of specificity shown by oxides for particular metals (Kinniburgh et al; 1976).
3. Changes in the surface charge properties of the oxides as a result of adsorption (Stumm and Morgan, 1981).

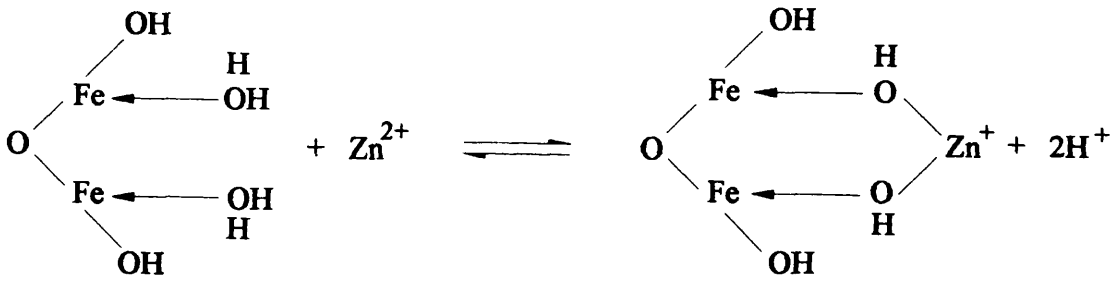
The last effect is attributed to the increased surface positive charge developed by chemisorption. For example, on goethite, the proposed surface reaction is

$$-Fe-OH + M(H_2O)_6^{2+} \longrightarrow -Fe-O-M(H_2O)_5^{+} + H_3O^{+}$$

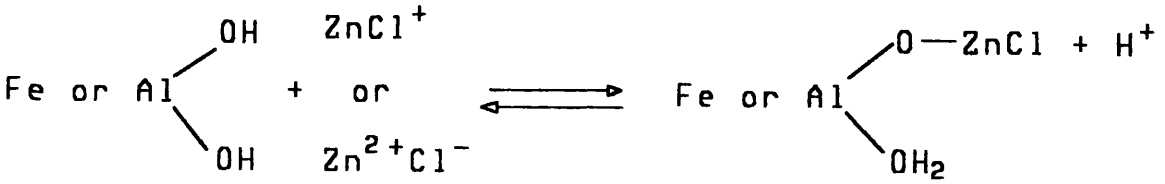
and can be detected as a change in electrophoretic mobility of suspended oxide particles.

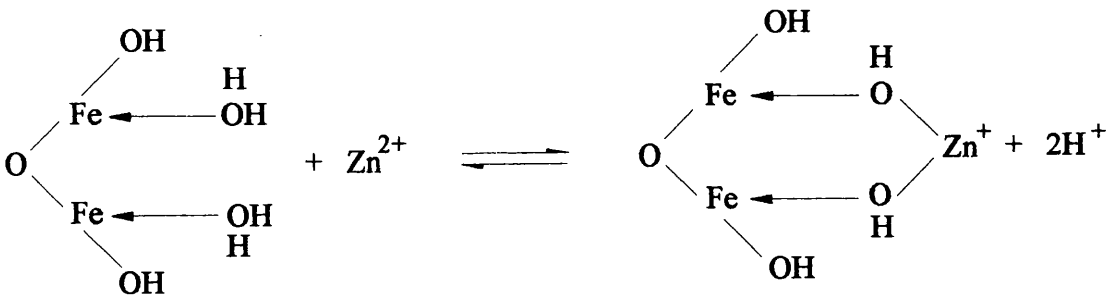
McLaren and Crawford (1973b) reported from their study that organic matter and free manganese oxides were the dominant constituents contributing towards specific adsorption 0f copper in soils. They found the adsorption maxima of copper on various soil constituents as in the following order

manganese oxides> organic matter> iron oxides> clay minerals. They also suggested that specific adsorption was the most important process in controlling the concentration of copper in soil solution. Knezek and Ellis (1980) mentioned that a strong adsorption of Zn by clay , that could not be reversed by use of neutral salt extraction has been reported by many research workers. The mechanism of the adsorption is unknown, but possible explanations ranged from octahedral layer substitution to specific binding sites. Quirk and Posner (1975) proposed a model that the adsorption of Zn(II) at an oxide surface may be represented as a bridging ligand between the neutral sites:



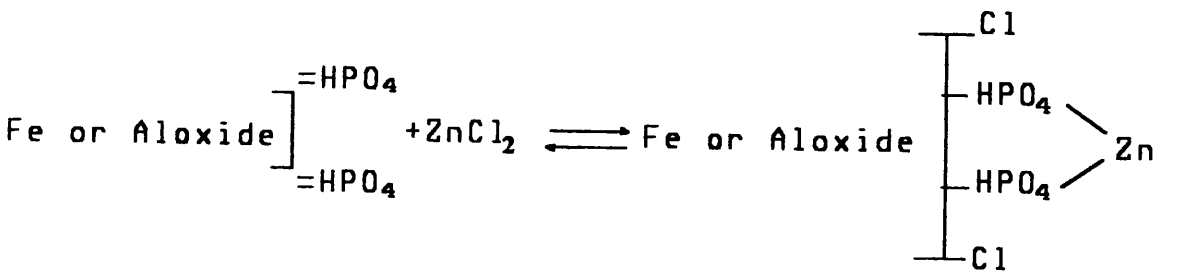
They observed such adsorption can be viewed as a growth or an extension of the surface and its properties would accord with the lack of complete reversibility. Kalbasi et al. (1978) later suggested two possible mechanisms for zinc adsorption by aluminium and iron oxide surfaces:





Their study shows that specific adsorption involved the adsorption of Zn^{2+} and release of two H^{+} ions for each mole of Zn^{2+} adsorbed and accounted for 60-90 percent of total zinc adsorption by Fe_2O_3. They further stated that specific adsorption of zinc by Al_2O_3 and Fe_2O_3 may be responsible for the frequently reported fixation and unavailability of zinc added to soils.

Stanton and Burger (1967) reported from a study that various hydrous oxides of iron and aluminium can sorb zinc through the medium of adsorbed polyvalent phosphate ions, which has been shown as follows:



They further showed from their results that zinc bound to hydrated iron oxides in soil through this mechanism is unavailable to plants. Diaz et al. (1990) reported that for a given P concentration, the amount of zinc adsorbed increased with pH and, at pH values above 6, more than 99% of total zinc in solution was taken up by the iron oxide. In soils with a low organic matter content or a high content of Fe, Al, and Mn oxides, the mineral fraction becomes important in governing adsorption (Pulford et al; 1982).

Gerhard et al. (1983) concluded from their model experiment in $CaCO_3$-buffered system, that the adsorption capacity for specifically adsorbed zinc (mole g^{-1}) by the following components increased in the order $CaCO_3$ (0.44), bentonite (44), humic acid (842), amorphous Fe- and Al-oxides (1190,1310) and MnO_2 (1540) and demonstrated the importance of Mn-,Fe-, and Al-oxides and humic substances

for the binding of zinc in soils containing carbonates, and thus indicated the special role of these components limiting precipitation reactions.

1.2.4 Metals associated with organic matter

Although metal bonding on organic matter can be viewed as an ion exchange process between H^+ and metal ions on acidic functional groups, the high degree of selectivity of organic matter for certain metals strongly suggests that some metals coordinate directly (i.e; form inner-sphere complexes) with the functional groups (studied by Schnitzer and Skinner, 1966, 1967). A typical affinity sequence of organic matter for metals (at pH 5) is given by Stevenson and Ardakani (1972) in the order as follows:

Cu> Ni> Pb> Co> Ca> Zn> Mn> Mg

but these sequences are commonly inconsistent, dependent on the nature of the organic matter, the method used to measure metal bonding, and the pH at which bonding is measured.

Hodgson et al. (1966) reported that more than 98% of the copper in solution was in an organic complexed form and Ellis and Knezek (1972) have reviewed literature that showed the existence of stable copper complexes with soil organic matter.

Lewis and Broadbent (1961a) used a series of phenolic and carboxylic acids as models and suggested that copper was adsorbed as $CuOH^+$ by carboxyl group whereas phenols bound Cu^+. Unfortunately, the use of actual

organic extacts in subsequent research did not clearly identify the forms of Cu bound, but did confirm the importance of carboxyl and phenolic groups in binding copper to organic matter (Lewis and Broadbent, 1961b; Schnitzer and Skinner, 1966).

Stable complexes of zinc with soil organic matter components have been known for a number of years. Randhawa and Broadbent (1965), Schnitzer and Skinner (1966), and Hodgson (1963) have suggested that humic and fulvic acid fractions of organic matter are very important 1n zinc adsorption.

Lindsay (1972) observed two important ways by which organic matter can interact with zinc. First, soluble zinc can be mineralized and made available to plants. Second, zinc can be bound into organic constituents that are immobile in soils, constituting a fixation mechanism from which zinc is not readily released. Randhawa and Broadbent (1965) proposed at least three sites responsible for binding of zinc in soils. The least stable fraction of zinc was believed to be associated with phenolic (>OH) and weakly acidic carboxyl (-COOH) groups. The most stable fraction of zinc was linked to strongly acidic carboxyl (-COOH) groups, where less than 1% of the zinc was strongly bound, but the importance of this fraction is that it represents a preferential binding of zinc.

Shirwal and Deshponde (1984) found a positive and significant relationship ($r=0.648$) between adsorption maxima and organic carbon, which implies that organic fractions play an important role in the retention of zinc.

Desorption of transition and heavy metals from organic matter, a process involving displacement of organic ligands by water, has not often been studied. Data on rates of adsorption and desorption in peat indicate that those metals that bond strongly in organic matter (e.g; Pb^{2+}, Cu^{2+}) are most rapidly adsorbed and most slowly desorbed (Bunzl et al; 1976). Because greater heats of adsorption are expected for the inner -sphere complexes formed between organic ligands and metals such as Cu^{2+}, desorption necessarily requires that a large activation energy be overcome. Isotope exchange data reveal that the bulk of the adsorbed Cu^{2+} and Fe^{3+} on organic matter is labile over a period of one day (McLaren and Crawford, 1974; Sedlacek et al; 1987). James et al. (1983) concluded that $Al(H_2O)_6^{3+}$ is somewhat more labile, but ligand exchange reactions involving Al^{3+}-organic complexes in soil solution are measurably slow, on the order of minutes to hours.

1.2.5 Precipitates of metals

In considering chemical equilibria, the precipitation of compounds is important. Certain anions in soils or soil solutions are likely to be associated with the transition metal-oxides, hydroxides, carbonates, and sulphides. Though precipitates containing these four anions are important in their place, yet other reactions may be equally important

Divalent Mn precipitates with hydroxyl ions according to the following equation:

$Mn^{2+} + 2OH^- \longrightarrow Mn(OH)_2$ pk=13.01

Manganese is one element that undergoes oxidation and then precipitation as an oxide. Thus both soil properties, pH and redox potential, influence the formation of insoluble oxides of manganese. The following equation illustrates the formation MnO_2 (Knezek and Ellis, 1980).

$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-$

Knezek and Ellis (1980) found that copper hydroxide forms readily in aqueous media if sufficient Cu^{2+} is present and pH of the solution is increased. Heating the solution containing the precipitate usually causes it to convert to the oxide. They further concluded that zinc hydroxide is so soluble that it is not considered to be important in soil. Even at pH 8 more than 1ppm Zn^{2+} would exist in a solution in equilibrium with $Zn(OH)_2$. The tendency for $Zn(OH)_2$ to form is less than for $Cu(OH)_2$. They also suggested that in acid media hydrogen ions react with reduced sulphur species to form the very stable H_2S. But under reducing conditions with pH values greater than 7, metal sulphides readily form.

Dhillon et al. (1981) reported that some of the copper precipitated as either copper hydroxide or carbonate when the concentration of added copper was greater than 100 M. They were working on some alkaline soils of north west India which had high pH and carbonates. They suggested that clay or carbonate mineral surfaces in these soils acted as nucleation sites for precipitating copper.

Zinc and copper concentrations diminish in flooded soils (Iu et al; 1981 a,b), as soluble Fe and Mn increase, which has been proposed to indicate ferrite formation (Pulford, 1986). Similar observations were later supported by Sajwan and Lindsay, 1986. They proposed that the raised pH resulting from chemical reduction processes in acid soils could in itself be responsible for part of this effect, additional processes appear to be lowering the extractability of these metals. Suggested explanations include the formation of a fresh Fe or Mn oxide surface in intermittently waterlogged soil, that have high adsorptive capacity for the metals or the coprecipitation of Fe with metals to form ferrites such as $ZnFe_2O_4$ or $CuFe_2O_4$.

Shuman (1977) observed that zinc precipitated as $Zn(OH)_2$ at pH 8, causing the sharp apparent increase in zinc adsorption by iron and aluminium oxides. Pulford (1986) suggested that the concentration of zinc in solution could be controlled by a precipitation mechanism. Gupta et al (1987) reported that precipitation reactions controlled the solubility in alkali soil.

Major natural sources of the eight micronutrients and their suggested contents in a representative humid region surface soil are summarized by Brady (1990), as follows:

Table 1.4 Major natural sources of micronutrients in representative humid region surface soil

Element	Major forms in nature	Analyses of soils	
		Range	Surface soil
		(mg/kg)	(mg/kg)
Iron	oxides, sulphides and silicates	10,000 - 100,000	25,000
Manganese	oxides, silicates, and carbonates	20 - 4,000	1,000
Zinc	sulphides, carbonates and silicates	10 - 300	50
Copper	sulphides, hydroxycarbonates, and oxides	2 - 100	20
Boron	borosilicates, borates	2 - 100	10
Molybdenum	sulphides, oxides, and molybdates	0.2 - 5	2
Chlorine	chlorides	7 - 50	10
Cobalt	silicates	1 - 40	8

After Brady (1990) p. 384.

Major minerals of copper and zinc are listed below:

Copper: tenorite (CuO), malachite ($Cu_2(OH)_2CO_3$), azurite ($Cu_3(OH)_2(CO_3)_2$, chalcocyanite ($CuSO_4$), and cuperite (Cu_2O).

Zinc: zincite (ZnO), smithsonite ($ZnCO_3$), franklinite ($ZnFe_2O_4$), willemite (Zn_2SiO_4), zinkosite ($ZnSO_4$), and hopeite ($Zn_3(PO_4)_2.4H_2O$).

1.3 Factors affecting the availability of Micronutrient cations (trace metals).

Micronutrient cations such as iron, manganese, zinc,copper and cobalt are influenced in a characteristic way by the soil environment. Certain soil factors have the same general effects on the availability of these micronutrients to plants. These soil factors are soil pH, oxidation and reduction state, other inorganic reactions, antagonistic reactions and organic combinations (Brady, 1990).

1.3.1 Soil pH

The solubility of minerals in soil is greatly influenced by soil pH. The micronutrient cations are most soluble and available under acid conditions. In very acid soils there is a relative abundance of the ions of iron, manganese, zinc, and copper. Under acid conditions, the concentration of one or more of these elements often is sufficiently high to be toxic to common plants (Sillanpaa, 1982).

As the pH is increased, the ionic forms of the micronutrient cations are changed first to the hydroxy ions of the element and finally, to the insoluble hudroxides or oxides. The following example uses the ferric ion as typical of the group:

$$Fe^{3+} \xrightarrow{OH^-} Fe(OH)^{2+} \xrightarrow{OH^-} Fe(OH)_2^{+} \longrightarrow Fe(OH)_3$$

Simple cation (soluble) — Hydroxy metal cation (soluble) — Hydroxide (insoluble)

All of the hydroxides of the micronutrient cations are insoluble, some more so than others. The exact pH at which precipitation occurs varies from element to element and even between oxidation states of a given element.

The adsorption sites on oxides and organic matter are pH dependent (Randhawa and Broadbent 1965, Shuman 1975, Sims and Patrick 1978, and Cavallaro and Mc Bride 1984).

Kinniburgh and Jackson (1982) reported that zinc adsorption on iron hydroxide gel is pH dependent. They claimed that zinc adsorption at pH 6.5 was about 10 times greater than at pH 5.5.

Basta and Tabatabai (1992) reported that Cd, Cu and Pb adsorption maxima were significantly correlated (<0.05) with pH and base saturation. They also claimed that Ni adsorption maxima were not significantly correlated with any of the soil properties studied. Assaad and Nielsen (1984) studied some Danish arable soils for copper adsorption in relation to pH and concluded that the effect of soil pH on copper adsorption varied considerably amongst the soils examined, although, in general, there was an increase in adsorption with increasing soil pH and with initial copper solution concentration. Barrow (1986b) reported that zinc retention increased as pH increased. He assumed that $ZnOH^+$ ion was retained and the effect of pH was due to the increased proportion of this ion in solution.

Bansal (1985) revealed that adsorption of nickel increased up to the pH value 6.5 and then declined. He

attributed this change towards reduced competition from protons for active sites. Decrease in adsorption above 6.5 may be due to formation of nickel hydroxide.

1.3.2 Oxidation and reduction state (Redox reactions)

Oxidation-reduction reactions are those in which a chemical species goes from a more oxidized to a less oxidized (reduced) state, or vice versa. Two of the trace element cations are found commonly in soils in more than one valence state. These are iron and manganese. The lower valent states are encouraged by conditions of low oxygen supply and relatively higher moisture level. They are responsible for the change in sub soil colours, grays and blues in poorly drained soils in contrast to the bright reds, browns, and yellows of well-drained soils.

Biological activity can greatly alter the solubility of metals in soils by causing, directly or indirectly, changes in the oxidation state of metals. However, even cosidering the long- studied case of manganese oxidation in soils and natural waters, the importance of microbiological relative to chemical 'catalysts' of oxidation is difficult to assess (Davies, 1986).The availability of trace metals from organic matter mostly depends on the microbial activity, as they help in the degradation of organic matter. The most important microbiological effects on the availability of trace metals involve the oxidation and reduction of iron and manganese. Hodgson (1963) supposed five ways that

microorganisms may affect the availability of metals in soil:

(i) Releasing inorganic ions during the decomposition of organic matter.

(ii) Immobilizing ions by incorporation into microbial tissues.

(iii) Oxidizing a metal, generally to a less available form.

(iv) Reducing oxidized form of a metal under limited oxygen conditions.

(v) Indirect transformations, changing pH or oxidation potential.

Zunino and Martin (1977b) reported that the microbial ecology of soil may markedly influence the maximum binding ability characteristics of the naturally occuring soil organic matter due to their effect on its formation or decomposition. They may strongly influence the metal translocation and availability in soils.

There is an unfortunate tendency to assume, in the absence of proof to the contrary, that soil-mediated redox processes are biological. Some of the known non-biological electron-transfer processes that can affect metal solubility in soils are now described. Their importance relative to microbial processes will depend on the specific chemical and minerological properties of the soil.

1.3.2.1 Oxidation of metals by metal oxides

Generally heavy metals are less soluble in their higher oxidation states. Therefore, the ability of manganese oxides (and to a lesser extent iron oxides) to directly oxidize metals or to catalyze metal oxidation by O_2 could provide a mechanism for lowering trace metal solubility. Several examples have been reported in the literature where manganese oxides reduce the solubility of metals by an oxidation process. These include the oxidation of adsorbed Co(II) to Co(III) (Dillar and Schenck, 1986) and Fe(II) to Fe(III) (Stumm and Morgan, 1981). According to Stumm and Morgan (1981) oxidation of Mn^{2+} is autocatalytic, so that manganese oxides show large apparent sorption capacities for Mn^{2+} that increase with pH. Murray (1975) had the same idea, however he further added that Mn^{2+} oxidation in aqueous is very slow below pH 8. Therefore, in the absence of Mn-oxidizing organisms, Mn oxides could have an important role in reducing the concentrations of Mn^{2+} in soil solution.

1.3.2.2 Dissolution of metals by organics

Organic molecules with the capability to complex with metals can highly increase concentrations of these metals in soil solution by dissolution reactions at mineral surfaces. (Manley and Evans, 1986; Pohlman and Mc Coll, 1986). Generally the metal complexing ability of the organic within the range of soil pH is a good indicator of its ability to adsorb to metal oxides and enhance mineral dissolution. Dissolution can be assisted by redox

reactions in which the organic reduces the metal ion at the surface. In the case of Fe oxide, the general reaction is:

Fe(III)-organic complex——> Fe(II) + oxidized organic

This reaction is prompted at low pH and is facilitated for Fe(III)-organic complex involving phenolic groups, (studied by Hider et al. 1981).

If molecular oxygen is present in soil solution, then the redox reaction is coupled to the reoxidation of Fe^{2+}:

Fe(II) + ¼ O_2 + organic——> Fe(III)-organic complex

and the Fe(III) is effectively recycled, acting as a 'catalyst' for the oxidation of organics by O_2 (Stumm and Morgan, 1981). However,if anaerobic conditions exist in soil solution, high concentrations of Fe^{2+} may accumulate.

A wide range of organic compounds can be oxidized at Mn-oxide surfaces. These include diphenolics (substituted and unsubstituted catechols, hydroquinones, and resorcinols), salicylic acid, pyruvic acid, oxalic acid, and fulvic acids (Stone and Morgan, 1984a, 1984b). The redox reactions with fulvic acids photocatalyzed, presumably by a similar charge-transfer mechanism to that proposed for synthetic Fe oxide-organic complexes. Some organics such as malate (Jauregui and Reisenauer, 1982) and glutamate (Traina and Doner, 1985a), are oxidatively decomposed by Mn oxides.

1.3.3 Other inorganic reactions

Micronutrient cations interact with silicate clays. First, they may be involved in cation exchange reactions much like those of calcium. Second, they may be more tightly bound or fixes to certain silicate clays, especially the 2:1 type. Zinc, manganese, cobalt, and iron ions are found as elements in the crystal structure of silicate clays. Depending on the conditions, they may be released from the clays or fixed by them in a manner to that by which potassium is fixed. The fixation may be serious in the case of cobalt, and sometimes zinc, because each element is present in soil in very small quantity (Brady, 1990).

1.3.4 Antagonistic reactions

When application of one element as a fertilizer to the soil reduces the availability of another important nutrient, it is said that an antagonistic reaction has happened. e.g; the application of large quantities of phosphate fertilizers can adversely affect the supply of the micronutrients. The uptake of both iron and zinc may be reduced in the presence of excess phosphates by making iron or zinc phosphates. From a practical stand point, phosphate fertilizers should be used in only those quantities required for good plant growth.

Lime-induced chlorosis (iron deficiency) in fruit trees is encouraged by the presence of bicarbonate ion. Bicarbonate- containing irrigation waters enhance the level of this ion in some soils. The chlorosis apparently

results from iron deficiency in soils with high pH, because the bicarbonate ion interferes in some way with iron metabolism (Brady, 1990).

Kawasaki and Moritsugu (1987) showed that addition of calcium to a test solution decreased the absorption of zinc, manganese, and cadmium, and also inhibited the translocation of cadmium in excised barley roots. Sajwan and Lindsay (1986) observed zinc deficiency in submerged paddy rice soils. They attributed this deficiency towards high solution concentrations of reduced Fe and Mn, which developed in paddy culture.

1.3.5 Organic combinations

Each of the five micronutrient cations may be held in organic combination. Microorganisms also assimilate the cations, which are apparently required for many microbial transformations. The organic compounds with which these trace elements are combined vary considerably, but they include proteins, amino acids, and constituents of humus, including the humic acids. Among the most important are the organic complexes, combinations of the metallic cations and certain organic groups. The complexes may protect the micronutrients from certain harmful reactions, such as the precipitation of iron by phosphates and vice versa. Soluble complexes increase micronutrient availability while insoluble ones decrease the availability. These complexes are called chelates.

1.4 Types of study on soil trace metals

An understanding of the mechanism by which the concentrations of trace elements in soil solution are controlled, is important in terms of their supply to plants and behaviour as soil pollutants. Many researchers now believe that there are instances where, in spite of soils being highly deficient in zinc and copper, crops have not shown considerable response to the added zinc and copper at the normal recommended rate. Keeping in view this problem, some processes are discussed in the following sections which are considered responsible of the availability of trace elements.

1.4.1 Adsorption / Precipitation study

Adsorption is the process through which a net accumulation of a substance occurs at the common boundary of two contiguous phases. The study of adsorption in soils is characterized by three laboratory operations that define the net accumulation of a substance at the interface between solid soil particles and a contiguous fluid: (1) reaction of the soil with a fluid of prescribed composition for a prescribed period of time, (2) isolation of the soil from the reactant fluid phase, and (3) chemical analysis of the soil and/or the reactant fluid phase (Sposito, 1984).

An adsorption study is done by putting the metal on to soil, which is opposite of soil extraction. It shows the amount of adsorbate (solute) sorbed as a function of its equilibrium concentration. A known amount of metal in

solution is equilibrated with known weight of soil at a constant temperature, and the amount adsorbed in $\mu g\ g^{-1}$ is determined by measuring the amount left in $\mu g\ cm^{-3}$ in the solution. Adsorption simply refers to when a chemical species passes from one bulk phase to the surface of another, where it accumulates without penetrating the structure of the second phase (Burchill, et al. 1981).

Precipitation can be defined as an accumulation of a substance to form a new bulk solid phase. Both of these concepts imply a loss of material from an aqueous solution phase, but one of them is inherently two-dimensional and the other is inherently three-dimensional. However, the distribution between the two begins to blur after one realizes the chemical bonds formed in both can be very similar, and that mixed precipitates can be homogeneous solids with one component restricted to a thin outer layer because of poor diffusion (Sposito, 1984).

In soils, the problem of differentiating adsorption from precipitation is made specially severe by the facts that new solid phases can precipitate homogeneously onto the surfaces of existing solid phases and that weathering solids may provide host surfaces for the more stable phases into which they transform chemically. When no independent data on which to base a decision are available, this loss of material to the solid phases in a soil can be termed simply 'sorption' in order to avoid the implication that either adsorption or precipitation is occuring (Sposito, 1984).

Shuman (1975) observed that the Langmuir adsorption isotherm was derived for the adsorption of gases on solids and has since been used also to describe the relationship between the adsorption of ions by solids and the concentration of the ion in solution. The Langmuir equation which he presented is:

$$c/(x/m) = 1/kb + c/b$$

where c= equilibrium concentration of adsorbate ($mg\ l^{-1}$)

x/m =amount adsorbed ($mg\ kg^{-1}$)

b= adsorption maximum ($mg\ kg^{-1}$)

k= a constant related to bonding energy ($l\ mg^{-1}$)

If adsorption data conform to the Langmuir equation, then plotting c/(x/m) versus c yields a straight line with a slope 1/b and intercept 1/kb. The Langmuir constant b is the reciprocal of the slope (1/b) and the bonding constant k is given by slope/intercept.

Harter and Baker (1977) critically examined the Langmuir adsorption equation and concluded that the equation which the soil scientists have been using is in the wrong form. The error is of no great importance when used to obtain a calculated adsorption maximum for comparison to other absorbent properties. However it does become important when used to understand adsorption dynamics and bonding strengths. The commonly reported curvilinear nature of c/(x/m) versus c plots was simply the result of not considering the effect of desorbed ions in the equilibrium solution. When the equation was corrected by considering desorbed ions, the isotherm became linear. In addition, the unit k of the Langmuir equation was not

simply related to the bonding energy of the adsorbed ion, but to the ratio of adsorbed and desorbed ion bonding energies.

If data do not conform to the Langmuir equation, the less demanding Freundlich equation can be used successfully. Bohn et al. (1985) mentioned that Freundlich found that adsorption data from many dilute solutions, could be fitted to an equation of the form;

$$x/m = kc^{1/n}$$

where k and n are empirical constants and other terms have been defined previously. The equation was originally empirical, without theoretical foundation. It implies, however, that the energy of adsorption decreases exponentially as the fraction of covered surface increases. The Langmuir equation, on the other hand, states that the energy of adsorption on a uniform surface is independent of surface coverage. The linear form of the Freundlich equation is:

$$\log x/m = 1/n \log c + \log k$$

The Freundlich equation has the drawback that it does not predict a maximum adsorption capacity. Despite the shortcoming, this equation is a common adsorption equation and is included in several models for predicting behaviour of pesticides in soil. Many researchers have used this equation for zinc adsorption studies in soils as well as by iron hydrous oxide gel (Sidle and Kardos 1977; Shukla and Mittal 1979; Jarvis 1981; Kinniburgh and Jackson 1982; Kurdi and Doner 1983; Assaad and Neilsen 1985; Sarkar et al; 1989).

In soil, adsorption is known to regulate the concentration of trace metal ions in soil solution. Trace metal adsorption study has great importance due to increased deficiency problems in some soils under certain conditions or the increasing toxicity problem by industrial activity and land application of sewage sludge in some areas. The adsorption of trace metals by soils has importance in determining their availability to the plant and their movement through the soil.

Many researchers have used different aspects for trace metals adsorption studies. Sidle and Kardos (1977) used forest soil for adsorption of copper, zinc, and cadmium and found that essentially all of the copper was adsorbed by the soil in the first 20 minutes of equilibration. Copper adsorption data fit the Freundlich isotherm better than the Langmuir isotherm. Adsorption of zinc and cadmium was more time dependent than copper, especially for 0-7.5 cm depth of soil. Biddappa et al. (1981) studied three typical soils of Japan under flooded condition for adsorption and desorption of heavy metals, and concluded that the sorption of all heavy metals was up to the maximum concentration (5000 $\mu g\ g^{-1}$ soil). The magnitude of sorption in general was in the order of Pb> Cu> Zn> Cd> Ni. Joshi (1986) used different textured arid soils for copper adsorption study, and suggested that sandy loam soils have higher values of adsorption maxima and bonding energy constants than sandy soils. Zinc adsorption studies on calcareous and alkaline soils, in which zinc deficiency is the most common problem, have

been conducted by Kuo and Mikkelson (1979), Dhillon et al. (1981) and Sigh and Abrol (1985). For acid soils which may produce toxicity of trace metals and which could be dangerous to plant, adsorption studies have been done by Saeed and Fox (1977), Kuo and Baker (1980) and Cavallaro and Mc Bride (1984).

Some soil scientists have approached the idea that pH has a great influence on the adsorption of trace metals and determined a decrease in zinc solubility with increasing pH (Saeed and Fox 1977, Mc Bride and Blasiak 1979, Harter 1983, and Gupta et al.1987).Brummer et al. (1983) reported that below pH 7 zinc concentration in soil solution is controlled by adsorption-desorption reactions with soil clay and whole soils. The adsorption of trace metals on solid phase surfaces, such as clay minerals and hydrous oxides, particularly iron and aluminium oxides, have been studied by Kinniburgh et al. (1976), Shuman (1976, 1977), Kalbasi et al. (1978), Inskeep and Baham (1983), Barrow (1986) and Mc Laren et al. (1986).

Shuman (1975) reported that zinc adsorption data for four soils conformed to the Langmuir adsorption isotherm, when the curves were resolved into two linear portions representing two different types of adsorption site. He also observed that the adsorption sites for the lower part had very high bonding energy coefficients and low adsorptive capacities compared with the adsorption sites of the part of the curve corresponding to higher zinc concentration in the equilibrium solution. Pulford (1986) used different salts as background electrolytes for zinc

adsorption by seven soils and described the split Langmuir isotherm in the same way as Shuman (1975). Dhillon et al. (1981) studied four alkaline soils of north-west India for the adsorption of copper by using $CaCl_2$ as supporting electrolyte. They concluded that the adsorption data conform to the competitive Langmuir adsorption equation although there was possibility of copper hydroxide or carbonate precipitation at higher concentrations of added copper. The adsorption capacities of soils were related to CEC, clay content and $CaCO_3$ equivalent of soil. The free energy change for adsorption and for interaction were negative and positive respectively.

Some workers used adsorption study to see the effects of different anions present in the equilibrating solution and the ionic strength of that solution. Chawla et al. (1985) used 0.05M $Ca(NO_3)_2$ and 0.1M $Mg(NO_3)_2$ solution as background electrolytes for zinc adsorption in Mollisols of Uttar Pradesh India. Kinniburgh and Jackson (1982) used 1M $NaNO_3$ solution as background electrolyte for zinc adsorption by iron oxides, and Shuman (1986) used 0.005, 0.01, 0.05 and 0.1M $NaNO_3$ for zinc adsorption by soils. Barrow et. al. (1981) studied the adsorption of copper, lead and zinc on goethite using a 0.075M chloride solution, 0.0075M chloride solution, a 0.075M nitrate solution and 0.0075M nitrate solution.

1.4.2 Desorption/dissolution study

The removal of sorbed materials from surfaces is called desorption which is opposite to the process of adsorption. Similarly the reverse process to precipitation is dissolution, and a considerable literature exists on the possible dissolution of sparingly soluble compounds into the soil solution.

Lindsay (1979) summarized the published data in this field. He described the solution concentrations of major and minor elements by the solubilities of definite compounds of these elements and by solubility graphs. The solution concentration of zinc in soils is explained by the solubility of an unknown zinc compound called 'soil-zinc' in relation to pH. Kittrick (1976) related it to ZnS in aerobic soils. Udo et al. (1970) attributed it to Zn-carbonate under specific conditions, while Zn-sulphate was found according to Kalbasi et al. (1978a). Many papers about trace elements in soils show that solution concentrations of these elements cannot be explained by solubility (Fassbender and Seekampt, 1976; Velk and Lindsay, 1977; Herms and Brummer, 1980), but are connected with adsorption-desorption processes and can be described by adsorption and desorption isotherms (Tiller et al; 1969; Gerth and Brummer, 1979).

Many researchers have used different extractants and electrolytes to desorb different trace elements in different ways to study the mechanism controlling the availability of these elements. Mc Laren et al. (1986) used 0.01M $CaCl_2$ solution as a background electrolyte for

cobalt desorption and concluded that cobalt sorbed by soil oxide material was not readily desorbed back into solution, and in addition, rapidly became non-isotopically exchangeable with solution cobalt. In contrast, cobalt was relatively easily desorbed from humic acid and the large portion of cobalt sorbed by humic acid remained isotopically exchangeable. Cobalt sorbed by montmorillonite was more easily desorbed than that sorbed by soil oxide but less easily desorbed than that sorbed by humic acid. Chawla et al. (1985) found different extractants varied in their capacity to desorb zinc according to the decreasing order DTPA> HCl> $Ca(NO_3)_2$> $Mg(NO_3)_2$. Chatterjee and Mandal (1985) reported that the amount of adsorbed zinc desorbed by H_2O, NH_4OAc and DTPA ranged from 0.7-6.5, 46.8-61.5, and 11.6-15.6%, respectively of the amount retained by different soils. This reveals that a major portion of adsorbed zinc is retained in the exchangeable form in the soils studied. They suggested that a portion of applied zinc which was retained by the soils were in form, other than exchangeable or chelated and may, therefore, be unavailable to plants. McLaren et al.(1983) studied some soils for Cu^{64} adsorption from solution on to samples of soil materials and concluded that the desorption isotherm obtained for the soil samples indicated that the amounts of copper readily desorbed from the humic acid and the soil oxides were very small. He further noted that greater amounts of copper were desorbed from montmorillonite. Maskina and Randhawa (1982) studied desorption of Zn^{65} in

six rice growing soils with its sequential extraction by various extractants. Average values of the zinc desorbed from the soils equilibrated with graded amounts of zinc (2.5 to 25μg ml^{-1}) by 0.05M $CaCl_2$, 0.1M $(MgNO_3)_2$, 0.001M EDTA and 0.1M HCl were 0.86, 0.43, 2.73, 4.95 and 2.16μg ml^{-1}, respectively. Higher values of coefficient of desorption (kd) and lower values of desorption maxima (Dm) in case of electrolytes suggest that they extract lower amount of sorbed zinc than complexing agents. Variations in the amount of chemical pools of zinc desorbed by different extractants may be related to pH, $CaCO_3$, clay fraction and other attributes of the soils. Biddappa (1981) desorbed heavy metals sequentially by extracting with 1N KNO_3, 0.005M DTPA and 1M HNO_3 for the evaluation of selective distribution of different chemical forms. He revealed that the desorption rate was greater than the adsorption rate indicating the predominance of the chemisorption over physical processes. The major portion of sorbed metals was retained in unextractable form, which overall accounted for more than 50% of the sorbed metals. He also pointed out that the desorption of nickel was quite different from other metal ions and the major portion (about 60 to 70%) of the applied nickel remained in the soil solution.

Padmanabham (1983) conducted adsorption-desorption studies using copper(II) as the adsorbate and synthetic crystalline iron oxide, goethite, as the adsorbent. These were carried out on the acid side of the isoelectric point (pH 7.5) in the presence of a large excess of indifferent

electrolyte. He found two types of adsorption sites for copper(II) on the oxide surface, one of low bonding energy and the other of high bonding energy, corresponding with the 'readily desorbed' and 'less readily desorbed' fractions of the cation respectively in his desorption experiments. He also suggested that the gradual interchange of some readily desorbed copper(II) into a category that is not readily desorbed after an initial 'time lag' between adsorption and desorption is attributed to a possible time-dependent reaction involving isomorphous substitution of lattice Fe^{3+} by Cu^{2+} of comparable ionic size.

1.5. Aims of the project

The main theme of this project is to understand better the chemistry and behaviour of trace metals in terms of their adsorption on soil, and desorption of the adsorbed elements by different dilution systems of desorbing agents to find out the maximum adsorption and desorption. The effect of temperature (activation energy) was also considered in this study. This study was carried out in order to explain the factors controlling trace metal availability to plants. Much attention has been given to zinc adsorption and desorption studies. Moreover, copper and nickel have been also investigated. The former two metals (Zn and Cu) with the idea of being important to plants and the later (Ni) being considered toxic to the environment and plants.

Chapter 2

Materials and Methods

2.1 Characteristics of study soils

The following five soils were studied which provided a wide range of some physical and chemical properties e.g; pH, organic matter, moisture content, cation exchange capacity etc. (Table 2.1).

1. Caprington
2. Amlaird
3. Dunlop
4. Midelney
5. Dreghorn

Caprington

The site is situated at West of Scotland College of Agriculture, Auchincruive, Ayr, Scotland. Grid No. is NS 376232. The soil is devoted to permanent grass and managed for grazing by dairy cows. The soil links to Rowanhill association which is developed from glacial till derived from sandstones and shales of the productive coal measures. This soil comes under the Caprington series which is classed as an imperfectly drained brown forest soil.

Amlaird and Dunlop

The site is located at South Drumboy farm, Fenwick, Ayrshire, Scotland. The Grid reference No. is NS 500484. The site is under permanent grass and used for sheep grazing and beef cattle. The site receives occasional dressing of lime. The soils belong to the Darleith association which is developed on till derived from carboniferous age igneous rocks (Basalt). The soil series are Amlaird and Dunlop. The former soil is classed as surface water gley while the later is known an imperfactly drained brown forest soil.

Midelney

The site is located at Bankfarm, Norfolk, England. The Grid reference No. is TF 588022. The soil is used for intensive arable crop production e.g; wheat, potatoes and sugarbeet. It belongs to Midelney series which is developed from calcareous alluvial clay parent material. The series has been classed as ground water gley.

Dreghorn

The site is situated at West of Scotland College of Agriculture, Auchin cruive, Ayr, Scotland. Grid reference No. is NS 373232. The soil

is under permanent grass adjacent to greenhouse . It belongs to the Dreghorn association which is developed from raised beach deposits. The series is Dreghorn which has been classed as freely drained brown forest soil.

Some physical and chemical properties of the study soils which were determined before initiating the actual project have been given in Table 2.1

Table 2.1 Properties of test soil

Soil series	pH water	pH $CaCl_2$	%LOI	CEC	% clay
Caprington	5.5	5.0	18.32	7.06	20
Amlaird	5.3	4.5	26.28	51.60	37
Dunlop	5.5	5.0	17.82	38.46	30
Midelney	6.3	6.0	11.92	28.80	40
Dreghorn	5.4	4.6	6.48	12.80	10

1. pH measured in given solution at given ratio using a combination of pH electrodes
2. Loss on ignition, at 450°C
3. Cation Exchange Capacity, in meK/100g has been described in section 2.4.1.

2.2 Analysis

For all experimental studies regarding this project, zinc, copper and nickel were determined by using flame atomic absorption spetrophotometry (Perkin-Elmer 370 A and 1100 B). Potassium was determined by emission method by atomic absorption spectrophotometry. All other requirements and standard conditions for determination of the above metals and potassium are given in Table 2.2

Table 2.2 Standard conditions for elements

Element	Wavelength (nm)	Slit setting (nm)	Range of standards (ppm)
Zn	213.9	0.7	0- 1.0
Cu	232.0	0.7	0- 5.0
Ni	341.5	0.2	0- 5.0
K	766.5	0.7	0-10.0

All dilutions of standards and samples were prepared in appropriate supporting solution or background electrolyte in the adsorption and desorption study to overcome the background interferences.

2.3 Cation exchange capacity

Duplicate samples of 10 g of air-dried <2mm soil were mixed with the same amount of acid washed sand poured into two glass columns plugged with small pieces of glass wool in them. After pouring acid washed sand-soil mixture some pieces of glass wool were placed lightly on the top. The columns were leached with 200 cm^3 1N potassium acetate at pH7 and the leachates discarded. Excess potassium acetate was removed by leaching both columns with 100 cm^3 90% ethanol and discarding the leachates. Then both columns were leached with 200 cm^3 1N ammonium acetate at pH7 and these leachates were collected in 250 cm^3 volumetric flasks. When all the ammonium acetate had leached through the columns then the flasks were made up to the mark with deionized water and mixed well. The concentration of

potassium in these solutions was measured using the flame photometer after diluting the extracted solution when necessary.

Cation exchage capacity is expressed as meK/100 gms of soil and milliequivalent are obtained by dividing the atomic weight in mgs by the valence of potassium.

2.4 Adsorption methods

2.4.1 Effect of shaking time on adsorption of zinc from 5 μg Zn cm^{-3} and 100 μg Zn cm^{-3} solutions as $ZnSO_4$

0.2 g soil in triplicate was treated with 10 cm^3 zinc solution from 5 μg cm^{-3} and 100 μg cm^{-3} in two different sets in four ounce glass bottles, and shaken in end-over-end shaker at room temperature. The shaking times were 0.5h, 1h, 2h, 8h, 12h, 24h, and 48 hours. After shaking for the required times the samples were filtered through filter paper no.2 (12.5 cm) and analysed by atomic absorption spectrophotometry. All dilution of standards and samples were prepared in deionized water. This method has been applied in Chapter 3 Section 3.2.

2.4.2 Zinc adsorption isotherm for five soils in water background

1 g of each of the five soils was shaken with 50 cm^3 from 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 $\mu g\ cm^{-3}$ in 4 ounce glass bottles on an end-over-end shaker for 18 hours. Soil suspensions were then filtered through filter paper no.2 (12.5 cm) into polythene bottles. Each filtrate was then analysed by atomic absorption spectrophotometer. Dilutions were done wherever it was necessary to bring the concentration of the samples in accordance to the standard readings. Moreover all the zinc standards were made up in deionized water. This method was applied in the experiment given in Chapter 3 Section 3.3.

2.5 Desorption methods

2.5.1 Desorption of added zinc by differential dilution at highest zinc concentration along with shaking duration from 0.5 h-20 days.

Replicate samples of 0.2 g of each soil was shaken with 10 cm^3 from 100 μg Zn cm^{-3} solution in 4 ounce glass bottles for 18 hours on an end-over-end shaker The samples were taken out and diluted with deionized water at one of the following

dilution factors, i.e., 0, x2, x3.5 x6 and x11 and shaken for a further 0.5h, 2h, 8h, 12h, 1d, 2d, 3d, 5d, 10d and 20 days. The suspension were filtered through filter paper no.2 (12.5cm) into polythene bottles and analysed by atomic absorption spectrophotometer. From this method we only derived the best shaking time of 18 hours for desorption of metals and this shaking time was frequently used in Chapter3, Chapter4 and Chapter5.

2.5.2 Desorption of added zinc by differential dilution of highest zinc concentration with deionized water after 18h shaking

Replicate samples of 0.2 g of each soil plus 10 cm^3 from 100 $\mu g\ cm^{-3}$ of zinc solution in 4 ounce glass bottles were shaken on a shaker at end-over-end position. The soil samples were then diluted with deionized water by all or part of the following factors, 0, x1.5, x2, x3, x4, x6, x8, x11 and x13 and shaken for a further 18 hours. The soil suspensions after 18 hours shaking were filtered through filter paper no.2 (12.5 cm^3) into polythene bottles and were analysed by atomic absorption spectrophotometer either. Dilutions to samples were done before analysis wherever it was needed. This method was used in chapter 3 Section 3.4.1.

2.5.3 Desorption of full adsorption isotherm of zinc by 2 times dilution

1g of each soil in replicate was shaken on a shaker at end-over-end position with 50 cm^3 of zinc solution taken from 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 μg Zn cm^{-3} in 4 ounce glass bottles for 18 hours. The samples were then diluted by 50 cm^3 deionized water and placed on the same shaker for further 18 hours shaking for desorption purpose. All the samples were analyzed by the same way as in the former procedures. The results obtained were described in Chapter 3 Section 3.4.2.

2.5.4 Desorption of middle part of isotherm by 0, x2, x5, x10 times dilution with deionized water

0.2g of each soil in replicate was shaken continuously with 10 cm^3 of zinc solution taken from 40, 50, 60, 70 and 80 μg Zn cm^{-3} respectively in 4 ounce glass bottles for 18 hours on a shaker at end-over-end position. Then each soil was diluted with the respective dilution factor and allowed further for 18h shaking for the desorption of metal. The filtrates were analysed by the same way as described in Section 2.5.2. The results obtained by

this procedure have been interpreted in Chapter 3 Section 3.4.3.

2.5.5 Desorption of zinc from 100 μg Zn cm^{-3} with 2 times and 6 times dilution with deionized water after different shaking times

0.2 g of each soil + 10 cm^3 from 100 μg Zn cm^{-3} solution in two sets, having 3 replicates for each soil was first shaken on the same shaker mentioned in the earlier procedures for 18 hours to get equilibrium in the solution Then both the sets were diluted by deionized water to the appropriate dilution factor i.e., one with 10 cm^3 and the other with 50 cm^3 deionized water. After this all the samples were allowed for the respective shaking timings allocated to them. These contact timings were 0.5, 1, 2, 8, 12, 24 and 48 hours. The samples were analysed by atomic absorption spectrophotometry and the data obtained were computed only to get appropriate shaking time for desorption studies. An 18 hours contact time for desorption of metals was concluded the appropriate time. This was then selected for further studies of desorption in Chapter 4 and 5.

2.6 Adsorption/desorption methods for Zn, Cu, Ni using 0.1M $NaNO_3$ solution as a background electrolyte

In this study three metals were taken into account and the same five soils were used. Stock solutions of 5, 10, 20,30, 40, 50, 60, 70, 80, 90, 100 $\mu g\ cm^{-3}$ for all the three metals were prepared from their salts in 500 cm^3 flasks in 0.1M $NaNO_3$ solution. Both the adsorption and desorption methods are similar to those mentioned in Section 2.4.2 and Section 2.5.2. The only difference is the 0.1M $NaNO_3$ as a background electrolyte here instead of deionized water. The data obtained from these methods were analysed by Langmuir and Freundlich isotherms and equations. The observations and results have been interpreted in Chapter 4 Sections 4.2.2 and 4.3.2.

2.7 Temperature effect on the adsorption of zinc in soils

Five soils mentioned in Section 2.2 were taken in this study for zinc adsorption at set temperatures (5, 10, 20, 25°C) and to determine activation energy involved. Three different concentrations of zinc (60, 180, 200 $\mu g\ cm^{-3}$) were used.

1g of each soil in three replicates in 4 ounce glass bottles were shaken with 0.1M $NaNO_3$ solution at 180 r.p.m. for 1.5 hours in orbital shaker at different set temperatures in order to attain pre-equilibration in solution. After pre-equilibration, 25 cm^3 of the different zinc concentrations were added to the samples inside the orbital shaker to avoid the effect of outside temperature and then the shaker was run for further 18 hours. The samples were then filtered through filter paper no.1 and collected in polythene bottles. The samples, after being diluted where needed, were analyzed by atomic absorption spectrophotometry. The data derived from this experiment were treated as Temperature (T) versus amount adsorbed in $\mu g\ g^{-1}$ (x) and log x versus 1/T for all soils. The activation energy was calculated from the regression of log x versus 1/T from the Arrhenius equation;

$$\log k = \text{const.} + \text{slope}(1/T) \text{ or } k = A \exp(-Ea/RT)$$

and

$$\text{slope} = -Ea/2.303xR$$

where 'Ea' is activation energy, 'R' is the gas constant in Kcal/mole, 'T' the absolute temperature (k), and 'A' is a constant.

The results have been discussed and interpreted in Chapter 5 Section 5.2.2.

2.8 Effect of temperature on the desorption of zinc in soils

0.2 g of each soil was pre-equilibrated with 5 cm^3 of 0.1M $NaNO_3$ solution in 4 ounce glass bottles in orbital shaker at 180 r.p.m. at different set temperatures in three sets, having three replicates each. Then to each set 5 cm^3 of zinc solution from 200 $\mu g\ cm^{-3}$ was added without taking the samples out to minimize the effect of room temperature. The samples were shaken further for 18 hours to attain the equilibrium between the zinc in liquid phase and zinc on solid phase. The samples after this period were diluted with 0.1M $NaNO_3$, one set with null dilution, the other with 10 cm^3 and the third with 50 cm^3 inside the shaker and shaken for 18 hours more to desorb the metal. The samples were analysed and the data were calculated by the same way as described in Section 2.7. The results obtained from this study have been interpreted in the Chapter 5 Section 5.3.2.

Chapter 3

Procedures for studying adsorption/desorption of zinc by soil

3.1 Introduction

The availability of zinc in soil is conditioned by adsorption, desorption, precipitation, dissolution, chelation and transport of the ions from soil to root surface. A knowledge of adsorption by soils and clays, mobility of solid phase zinc and reactions of complexing agents with zinc is necessary for a meaningful evaluation of the zinc supplying power of a soil (Khasawneh 1971, Sidhu et al.1977). The adsorption and release patterns of zinc are greatly influenced by the type of soil and its characteristics.

The composition of the solution phase is one of the most important properties of soils as many processes are connected with the movement of dissolved substances. Plants take up nutrients from the soil solution, so the concentration of dissolved nutrients is a characteristic value of the nutrient status of the soils. But the processes which determine the concentration of the different elements in the soil solution are not yet fully understood. Changes in soil water content, departures from equilibrium or steady state to non- equilibrium conditions, changes in pH, changes in the activity of microorganisms which influence redox conditions, contents

of soluble chelating agents and composition of soil atmosphere require simultaneous consideration. These processes moderate the reaction of adsorption-desorption, precipitation-dissolution and complex and ion pair formation in relation to the pH, and thus influence the composition of both the solid material and the soil solution.

For a very long time scientists have been trying to develop procedures for studying adsorption-desorption reactions of zinc with the aim of improving our understanding of plant availability, and still this work is going on. Due to the very intricate reactions within soil, more study on this aspect is needed and hence this study on development of different procedures for adsorption-desorption of zinc is one effort towards understanding this important phenomenon in soil.

3.2 Effect of shaking time on zinc adsorption by soil.

3.2.1 Method

In this study two different initial concentrations of zinc in solution were taken i.e. 5μg cm^{-3} and 100 μg cm^{-3}, and 7 shaking times were used. Full method description has been given in chapter 2 section 2.4.1.

3.2.2 Results and discussion

Tables 3.1 and 3.2 represent the zinc concentration in μg cm^{-3} retained in solution after different shaking times in Caprington, Amlaird, Dunlop, Midelney and Dreg-

TABLE 3.1 Effect of time contact in soils with 5 μgZn cm^{-3} on zinc adsorption in five soils.

Zn concentration in soil solution left after shaking (Means in $\mu g\ cm^{-3}$)

Hours	Caprington	s.d	Amlaird	s.d	Dunlop	s.d	Midelney	s.d	Dreghorn	s.d
0.5	0.20	0.011	0.27	0.025	0.13	0.020	0.12	0.000	0.47	0.012
1.0	0.19	0.010	0.26	0.011	0.10	0.021	0.10	0.006	0.43	0.000
2.0	0.20	0.010	0.24	0.000	0.09	0.012	0.10	0.006	0.42	0.017
8.0	0.17	0.006	0.22	0.006	0.09	0.026	0.10	0.006	0.40	0.025
12.0	0.18	0.000	0.22	0.006	0.08	0.000	0.13	0.010	0.38	0.010
24.0	0.16	0.006	0.21	0.01	0.10	0.012	0.13	0.017	0.40	0.030
48.0	0.15	0.006	0.18	0.006	0.10	0.010	0.13	0.010	0.34	0.015
LSD 0.05=	0.017		0.025		0.035		0.020		0.038	
LSD 0.01=	0.025		0.038		NS		0.029		0.057	

NS denotes non significant at given probability.

s.d = standard deviation

TABLE 3.2 Effect of time contact in soils with 100 μgZn cm^{-3} on zinc adsorption

Zn concentration in soil solution left after shaking (Means in $\mu g\ cm^{-3}$)

Hours	Caprington	s.d	Amlaird	s.d	Dunlop	s.d	Midelney	s.d	Dreghorn	s.d
0.5	43.3	5.77	36.7	2.89	41.8	0.76	15.0	0.00	66.7	5.77
1.0	40.0	0.00	35.0	0.00	41.0	1.00	11.7	2.89	60.0	0.00
2.0	40.0	0.00	33.3	2.89	38.8	1.44	13.3	2.89	60.0	0.00
8.0	40.0	0.00	33.3	2.89	37.8	1.26	8.3	2.89	60.0	0.00
12.0	40.0	0.00	30.0	0.00	37.3	1.16	10.0	0.00	60.0	0.00
24.0	33.3	5.77	30.0	0.00	35.8	1.26	10.0	0.00	63.0	5.77
48.0	33.3	5.77	31.7	2.89	32.3	0.58	10.0	0.00	60.0	0.00
LSD 0.05=	8.0		4.6		2.3		4.0		NS	
LSD 0.01=	NS		6.9		3.5		6.0		NS	

NS denotes non significant at given probability.

s.d = standard deviation.

ghorn soils. All the soils showed a significant difference between the concentration of zinc left in solution after different shaking times at the low initial concentration of zinc (5μg cm^{-3}). With the exception of Dunlop soil all other soils showed significant difference among the means at .01 level of probability.

At the higher concentration of 100 μg Zn cm^{-3}, Dreghorn soil gave no significant response to shaking times. In the rest of the soils significant differences were found in the concentration of zinc left in solution after shakings (table 3.2). The reaction of adsorption at both concentrations in all the soils was rapid with 0.5 hour treatment, then it gradually slowed with increasing shaking time. These results are in conformity with results of Mckenzie, 1972 and Bunzl et. al; 1976, who reported that copper adsorption by soil materials takesplace fairly rapidly, certainly within a few hours. However adsorption sometimes continues slowly after the initial rapid adsorption phase (Mckenzie, 1972; Cavallaro and McBride, 1978). Similar results have been concluded by Krishnasamy et al. (1989) while working on sixteen soil samples (0-25cm) from Tamil Nadu, India. They stated that Zn adsorption patterns were characterised by an initial fast reaction followed by a slow one. This is due to slow diffusion of zinc into the solid phase of the soils. Saeed and Fox (1979) and Kuo and Mikkelsen (1979) supposed that zinc adsorption was substantially complete after 24 hours shaking, although equilibrium was not attained until 72 hours had elapsed. Similarly Bakhsh (1988) observed

enhancement of zinc adsorption in soils while working on some soils to see the effect of two shaking times. He suggested that the length of shaking time enhanced the zinc adsorption due to better equilibration of soil with zinc solution .

3.3 Procedure for measurement of a zinc adsorption isotherm in water back ground

3.3.1 Method

This study was carried out for five soils using water background for different zinc concentrations described in chapter 2 Section 2.4.2. The observed data have been treated in terms of adsorption mechanisms.

3.3.2 Results and discussion

Adsorption isotherms obtained by plotting the amount of zinc adsorbed (x) per gram of soil versus concentration of zinc (c) remaining in solution at equilibrium have been represented in figure 3.1. The differences they showed in zinc adsorption revealed the order of zinc adsorption Midelney > Amlaird $\geq$ Dunlop > Caprington = Dreghorn. The observed data show that zinc adsorption was greater in the clayey soils than in the sandy soils. Shukla and Mittal (1979), Bakhsh (1988) and Krishnasamy et al. (1989) observed that more zinc was adsorbed by a loam soil than sandy soil. Nielsen (1990) concluded that zinc adsorption in soil is related mainly to the content of humus, metal oxides and hydroxides and some clay minerals. He further

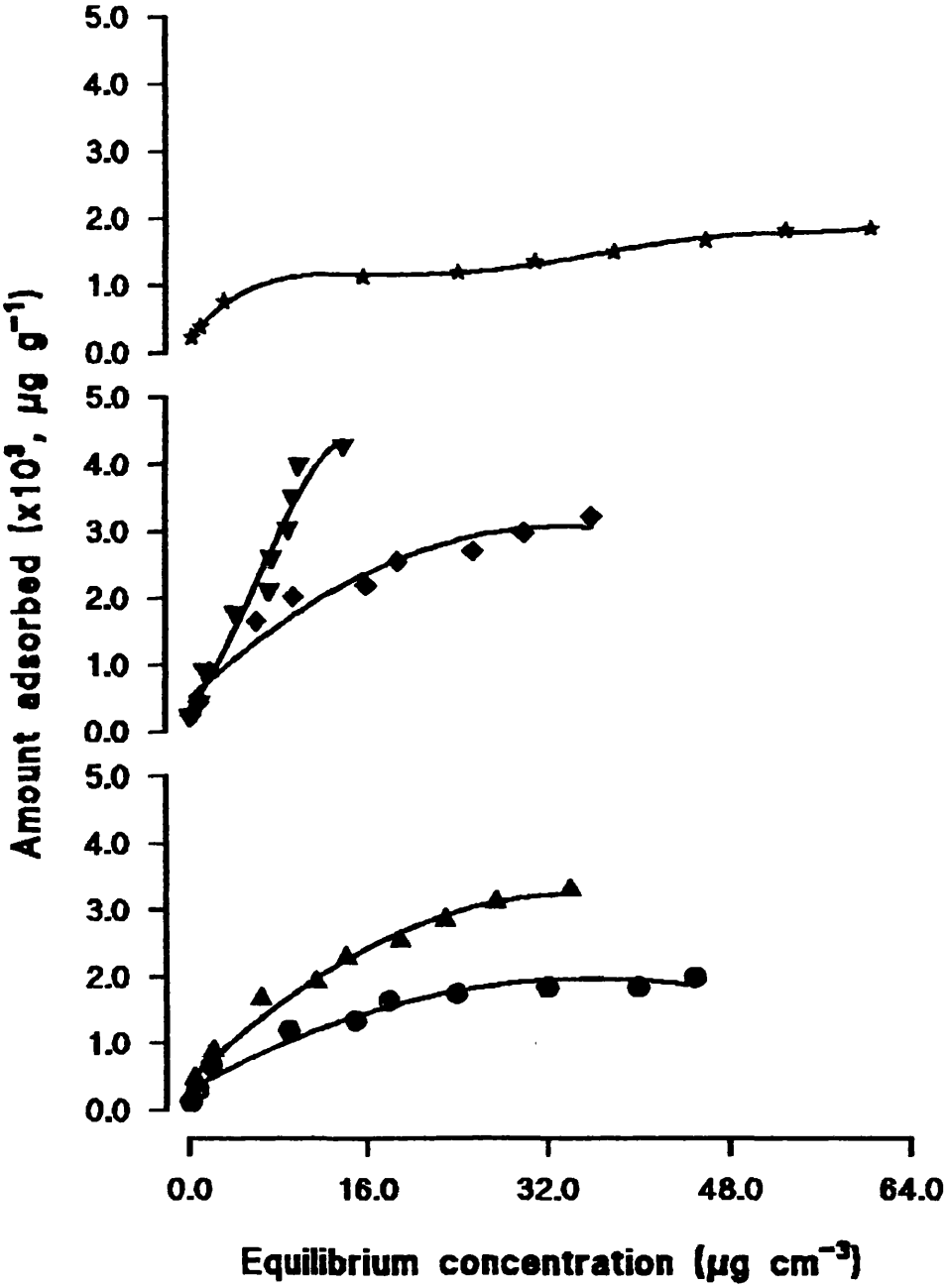


Fig. 3.1 Zn adsorption isotherms for 5 soils in water background.
(●) Caprington (▲) Amlaird (◆) Dunlop (▼) Midelney
(★) Dreghorn.

stated that the clay particle fraction is the principal adsorber of zinc compared to the other soil textural fractions. The effect of pH on the adsorption of zinc in these soils can not be ignored. For example the high pH of Midelney soil, along with its clayey nature, enabled this soil to retain 86% of added zinc from 100μg cm^{-3} zinc solution. These findings are well in conformity with the observations of Reddy and Perkins (1974) who observed a higher fixation of zinc at all levels of zinc application as the pH of a clay suspention was increased from 6.2 to 7.6. They further claimed that greater fixation of zinc at higher level was probably due in part to reduced solubility of zinc. One reason for higher amounts of zinc adsorption in Midelney soil in particular may be due to the retention of the univalent $Zn(OH)^{+}$ ion rather than the divalent Zn^{2+} ion at high pH. Harter (1983) reported that the increase in the ratio of univalent $Zn(OH)^{+}$ ions to the divalent Zn^{2+} ions from pH 6.0 to 8.0 would predict an approximately 60% increase in metal retention. Shuman (1975) observed that zinc adsorption was lower for sandy soils than for those high in clay. This observation well supports the results obtained for Dreghorn soil, which is sandy in nature and has a low pH and thus positioned itself in the lowest category of zinc adsorption.

Adsorption data were applied to the Langmuir equation, which in its linear form is:

$$c/x/m = 1/kb + c/b$$

This equation is discussed in chapter 1. The values of c/x versus c were plotted (fig 3.2-3.6) to fit the data

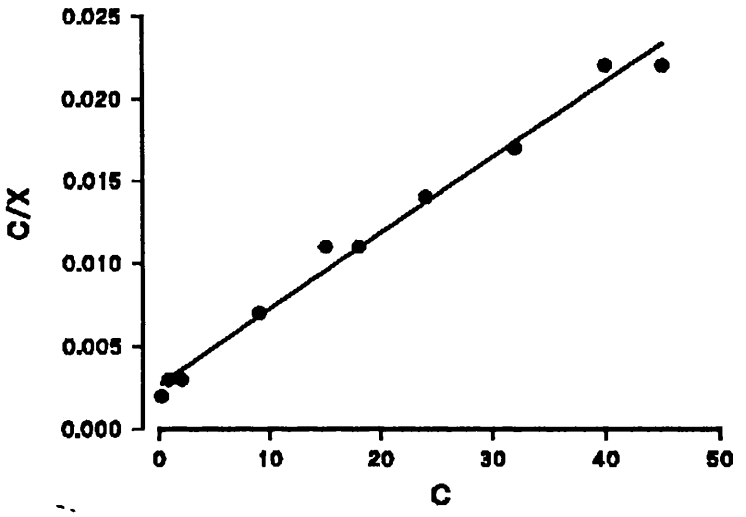


Fig. 3.2 Langmuir Isotherm for Caprington soil in water background.

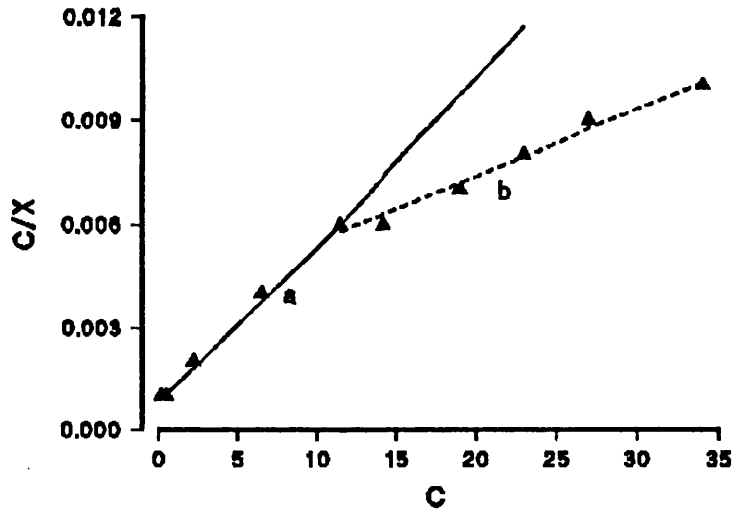


Fig. 3.3 a, b Langmuir Isotherm (split) for Amlaird soil in water background.

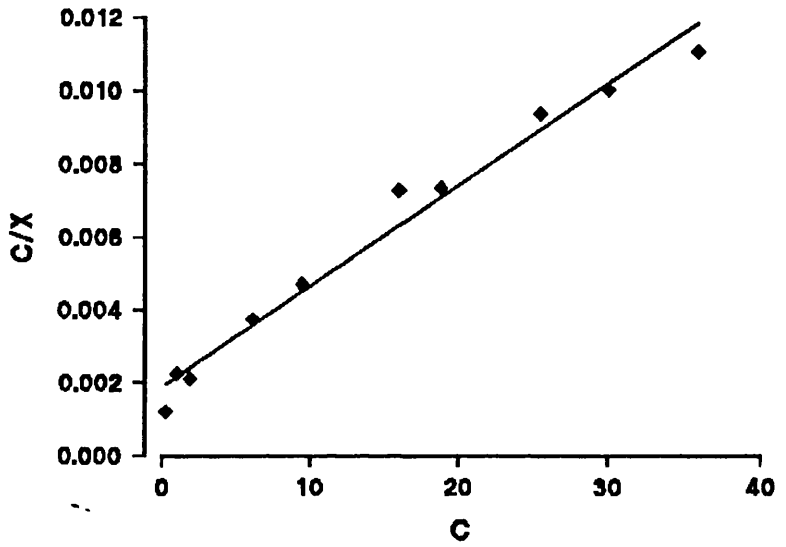


Fig 3.4 Langmuir isotherm for Dunlop soil in water background.

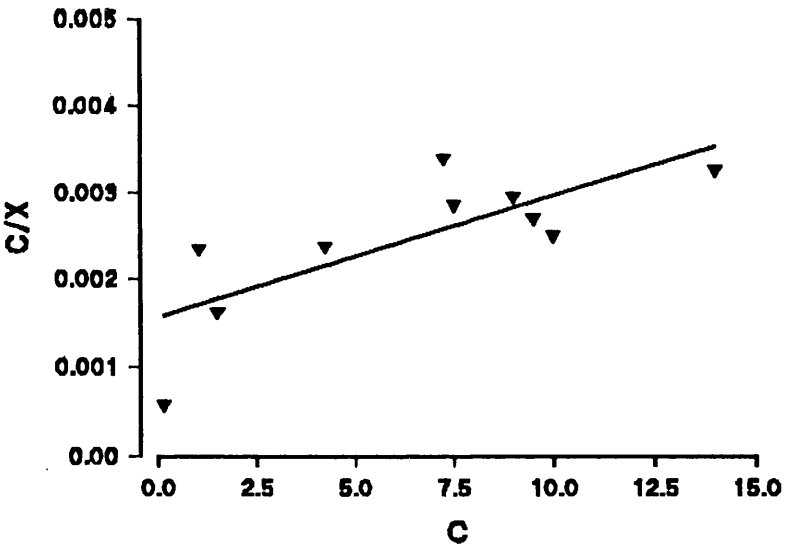


Fig. 3.5 Langmuir isotherm (scattered) for Mideiney soil in water background.

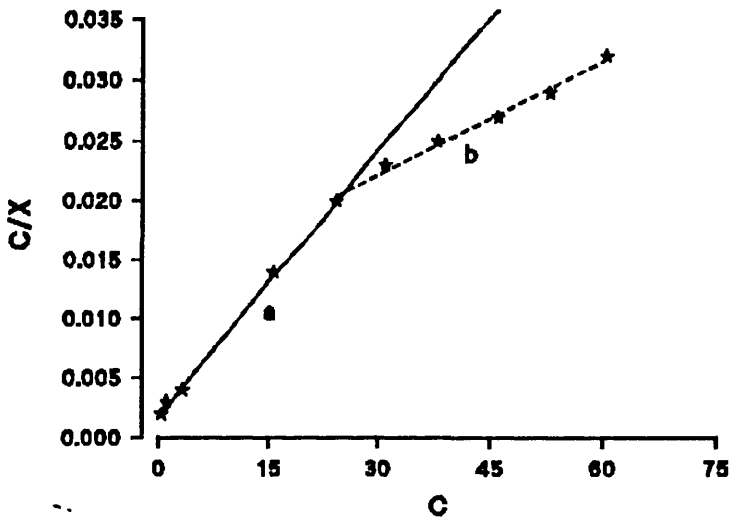


Fig. 3.6 a, b Langmuir isotherm (split) for Dreghorn soil in water background.

to the Langmuir isotherm. Different soils showed different response when the curves were resolved into a linear form. For example Caprington and Dunlop soils gave almost straight lines (fig 3.2 and 3.4) conforming to the Langmuir equation. These observations are well in order with those stated by Saeed and Fox (1979), Relan et al.(1980), and Sarkar et al. (1989). They fitted straight lines to their data either by applying Langmuir equation or Freundlich equation.

The Amlaird and Dreghorn soils showed an excellent fit when the curves were resolved into two linear portions (figs. 3.3 and 3.6). Shukla and Mittal (1979), Pulford, (1986) and Bakhsh (1988) used this approach to their data of zinc adsorption by soils, which did not conform to the simple Langmuir equation as it did not fit a single straight line. They claimed the resultant isotherms as split isotherms. The existence of two linear portions in the curves might indicate two types of adsorption sites or adsorption reactions as reported by Shuman (1975) and Shukla and Mittal (1979).

The most common way of resolving this deviation from a single straight line is to split the isotherm. The data in figures 3.3a and b and 3.6a and b lie on two straight lines.There is no reason to suppose that adsorption is restricted only to two surfaces, as suggested by Pulford (1986). A large number of surfaces, covering a range of bonding energies, are more likely to be found in soil. Two straight lines may only show the distribution of

experimental data. If there had been more points more evenly distributed, then a curve could have been a better description than two straight lines.

The Midelney soil did not conform to the Langmuir equation (fig 3.5). It showed scattered points which could not be fitted to a straight line. This may be due to the high affinity of the adsorbing sites in this soil towards adsorption of zinc with high bonding energy.

Posner and Bowden (1981) reported that it is erroneous to split the isotherms into a series of Langmuir isotherms unless there are good reasons, because the model which is based on a single type of adsorption site is closely similar to the experimental isotherms. Therefore if data fail to conform to the Langmuir equation, a less demanding equation can be used. Bohn et al. (1985) presented the linear form of Freundlich equation as below (see also section 1.4).

$$\log x/m = 1/n \log k$$

Experimental data were replotted according to this linear form of the equation (figures 3.7-3.11), and all the soils showed good agreement with the equation. Saeed and Fox (1979) observed the linear form of Freundlich equation while working on zinc adsorption by tropical soils influenced by phosphate fertilization. Sarkar et al. (1989) studied adsorption-desorption behaviour of zinc in some soils of Andhra Pradesh (India) and found that with an increase in the amount of zinc added, there was increase in equilibrium concentration, amount adsorbed, percent saturation, and supply parameter of zinc.

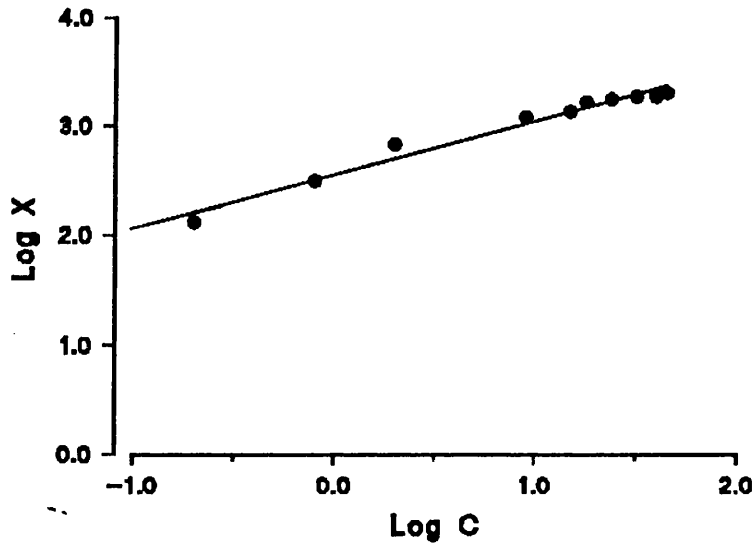


Fig. 3.7 Freundlich isotherm for Caprington soil in water background.

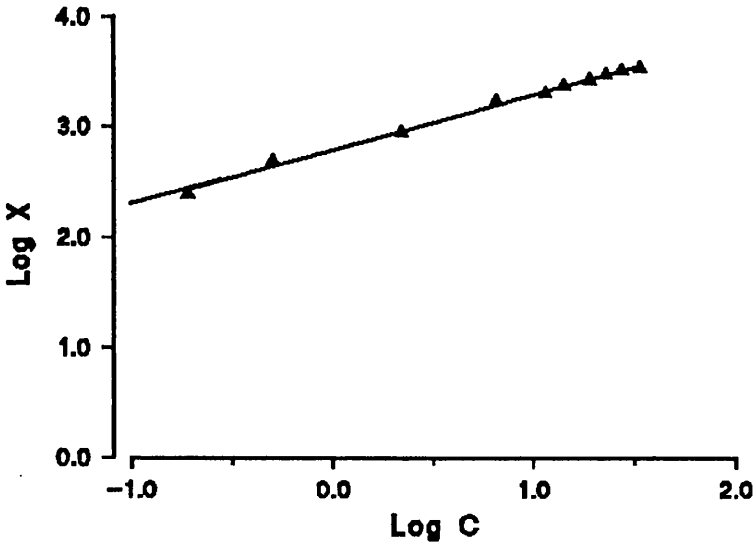


Fig. 3.8 Freundlich isotherm for Amlaird soil in water background.

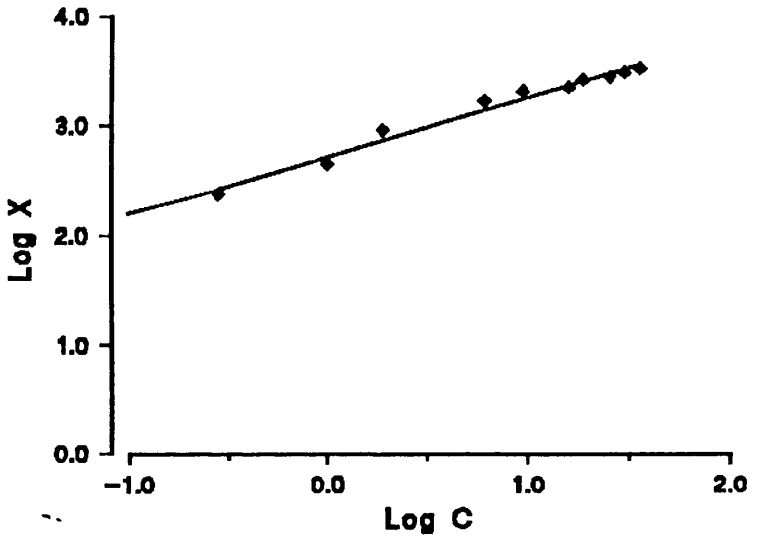


Fig. 3.9 Freundlich isotherm for Dunlop soil in water background.

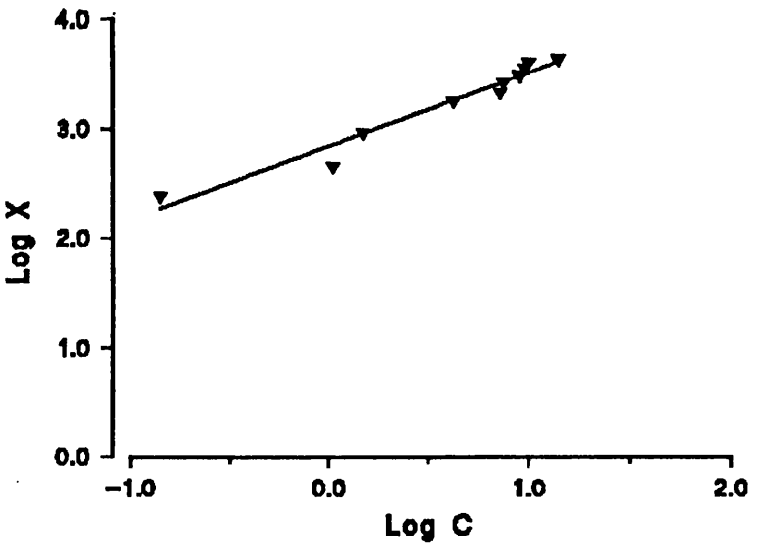


Fig. 3.10 Freundlich isotherm for Mideiney soil in water background.

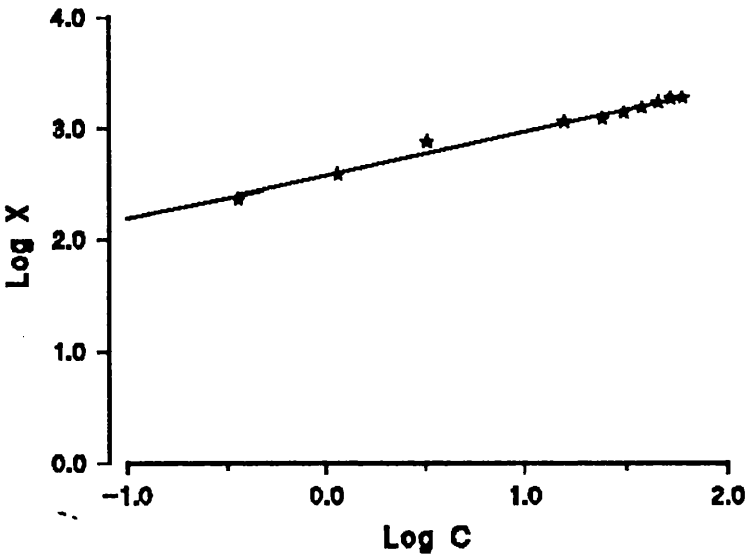


Fig. 3.11 Freundlich isotherm for Dreghorn soil in water background.

They suggested one kind of adsorption site in all the soils.

Zinc adsorption constants for the five soils were calculated from Langmuir as well as Freundlich plots and are given in table 3.3. The table shows that adsorption maxima in the soils were in the order Midelney > Amlaird> Dunlop > Dreghorn > Caprington, provided the top part of the isotherms for Amlaird and Dreghorn are included rather than full isotherms of these two soils. Generally the soils which had high clay content showed maximum adsorption capacity, e.g the order of adsorption maxima observed shows that Midelney soil, which has 50% clay (Pulford, 1986), indicated the highest adsorption maximum while the Dreghorn, which according to Bakhsh (1988) has 10% clay, presented the second lowest adsorption maxima, which is slightly higher than the adsorption maxima of Caprington. Bakhsh (1988) also observed the highest adsorption maxima in the Midelney soil and the lowest adsorption maxima in the Dreghorn soil while investigating zinc adsorption behaviour in some soils from Scotland and England.

The slope , intercept and R^2 values for each soil calculated from the Freundlich plots are also shown in Table 3.3. For all the soils very good R^2 was observed , the lowest R^2 (0.95) for Midelney soil and the highest R^2 (0.99) for Amlaird. The highest slope (0.67) was noted for Midelney soil and the lowest (0.39) for Dreghorn. These findings are in contradiction with the results of Sidhu et

TABLE 3.3 Zinc adsorption constants for five soils calculated from Langmuir and Freundlich plots in water background.

Soil		Langmuir plot			Freundlich plot		
		Adsorption maximum b mgg^{-1}	Bonding energy k $1mg^{-1}$	R^2	Slope	Intercept	R^2
Caprington		2.14	0.19	0.99	0.49	2.55	0.97
Amlaird	lower	2.26	0.45	0.98	0.49	2.78	0.99
	upper	5.17	0.05	0.99	-	-	-
Dunlop		3.75	0.15	0.98	0.54	2.72	0.98
Midelney		7.10	0.09	0.59	0.67	2.84	0.95
Dreghorn	lower	1.32	0.44	1.00	0.39	2.58	0.98
	upper	3.12	0.03	0.99	-	-	-

al. (1977) , who claimed that zinc adsorption isotherms for soils had slopes that increased as the texture of the soils became coarser.

3.4 Desorption procedures for removal of adsorbed zinc

In this study an effort has been made to desorb zinc with deionised water by applying different procedures already discussed in section 2.5. For this purpose preliminary experiments were carried out with the aim of determining an appropriate shaking time for desorption. Shaking times from 0.5h up to 20 days were observed for desorption, and finally 18h shaking time was selected to study desorption of zinc in the following procedures.

3.4.1 Desorption of zinc from 100 μg Zn cm^{-3} by differential dilution with deionized water

3.4.1.1 Method

The procedure has been discussed in Chapter2 Section 2.5.2. in detail.

3.4.1.2 Results and discussion

The zinc adsorption and desorption isotherms have been represented in figures 3.12-3.16 for all five soils. All the soils show that no zinc is desorbing at all with dilution. With the exception of Midelney soil all others indicated further adsorption of zinc. This means that the process of zinc adsorption in these soils is chemisorption

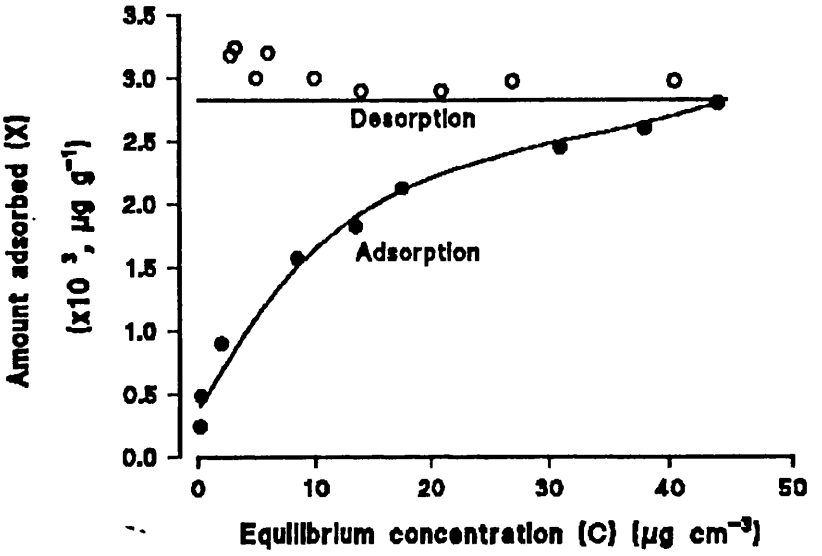


Fig. 3.12 Desorption of Zn from 100 µg Zn cm^{-3} by differential dilution with deionized water in Caprington soil.

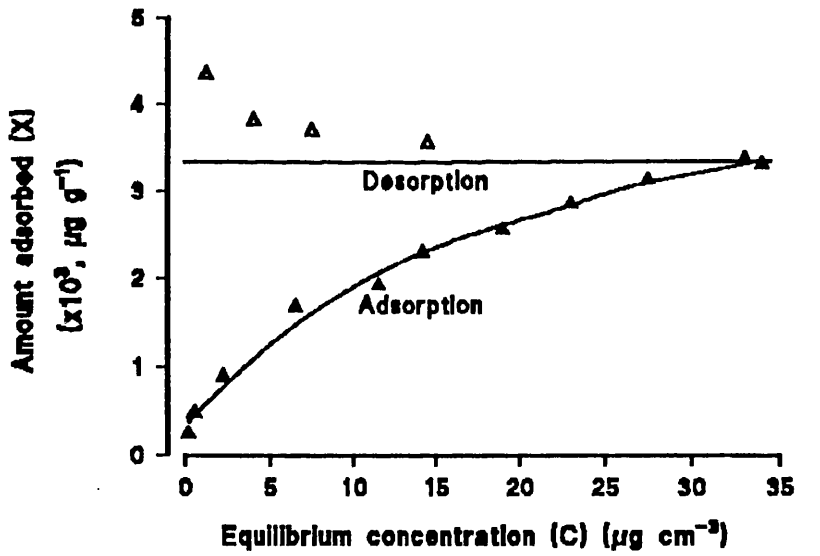


Fig. 3.13 Desorption of Zn from 100 µg Zn cm^{-3} by differential dilution with deionized water in Amlaird soil.

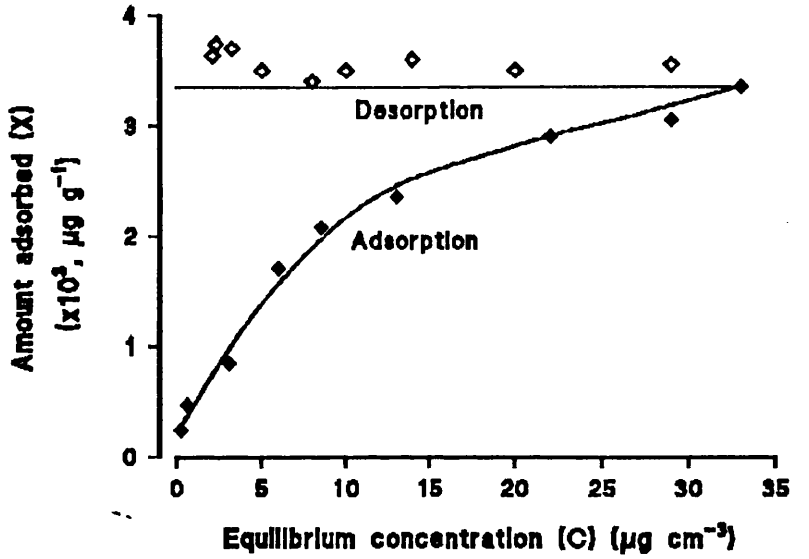


Fig. 3.14 Desorption of Zn from 100 µg Zn cm^{-3} by differential dilution with deionized water in Dunlop soil.

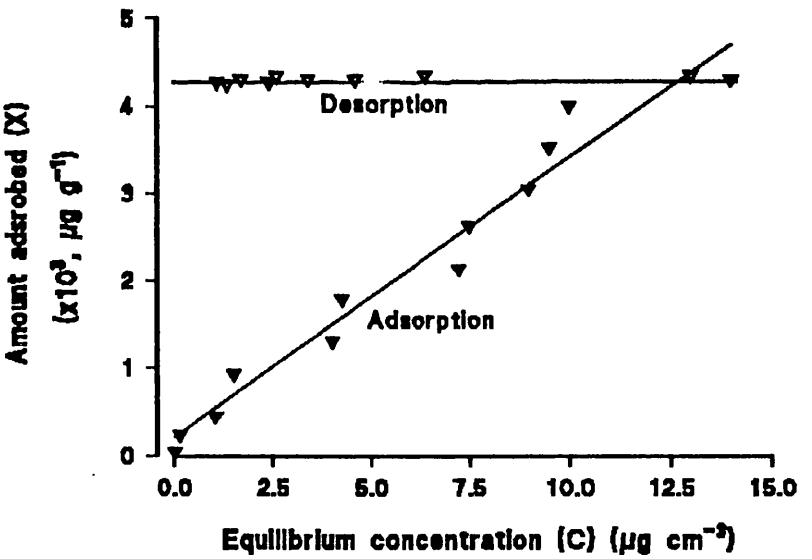


Fig. 3.15 Desorption of Zn from 100 µg Zn cm^{-3} by differential dilution with deionized water in Mideiney soil.

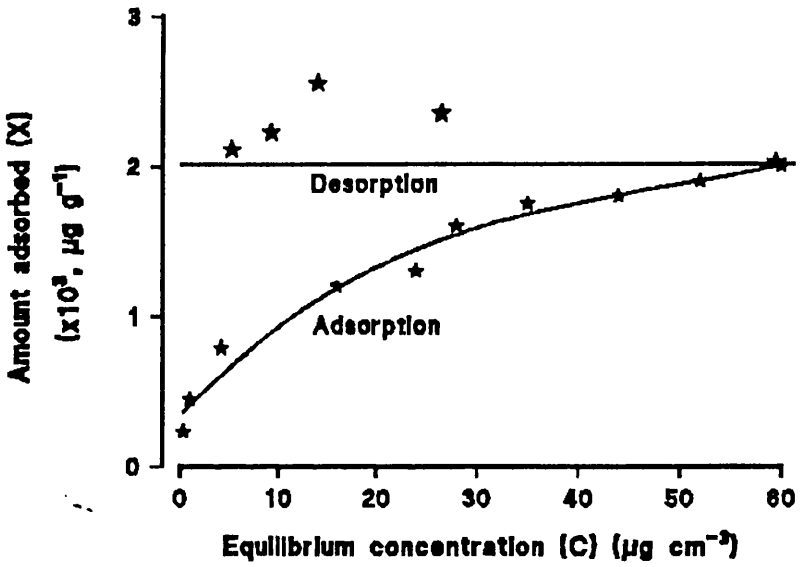


Fig. 3.16 Desorption of Zn from 100 µg Zn cm^{-3} by differential dilution with deionized water in Dreghorn soil.

based, suggesting very strong bonds of zinc with specific adsorbing sites or organic fractions and thus ruling out physisorption. The dilution by deionized water had no approach to the chemical process (reaction) to break those strong bonds. These observations are well supported by Sarkar et al. (1989) who studied adsorption-desorption behaviour of zinc in some representative soils of Andhra Pradesh, India. They concluded that deionized water could not desorb the adsorbed zinc, ruling out involvement of physical adsorption. As desorbing agent $CaCl_2$ was more effective than KCl, but neither KCl nor $CaCl_2$ could completely desorb the adsorbed metal, indicating the possibility of some being irreversibly fixed in the soil system

3.4.2 Desorption of full adsorption isotherm of zinc by 2 times dilution with deionized water

3.4.2.1 Method

See Chapter 2 Section 2.5.3

3.4.2.2 Results and discussion

The zinc adsorption and desorption data have been represented in Table 3.4 for the five study soils. It is evident from the Table 3.4 that no significant amount of zinc was recovered from all the concentrations with 2 times dilution with water, a very slight amount of zinc was obtained in solution from some initial low concentrations. Most of the soils showed a little

TABLE 3.4 Desorption of zinc from full adsorption isotherm diluted by 2 times with deionized water.

Soil		Weight of zinc in $\mu g\ cm^{-3}$ used										
		250	500	1000	1500	2000	2500	3000	3500	4000	4500	5000
Cap	Ads	235	480	906	1287	1537	1875	2075	2300	2450	2650	2750
	Re	10	15	11	24	NR	NR	NR	NR	NR	NR	NR
Aml	Ads	237	471	900	1283	1650	1966	2325	2583	2750	3016	3233
	Re	3	4	NR	NR	NR	NR	NR	NR	NR	NR	NR
Dun	Ads	238	471	950	1450	1850	2187	2512	2762	3050	3237	3488
	Re	NR	NR	44	40	70	88	128	NR	NR	NR	NR
Mid	Ads	245	491	981	1462	1930	2390	2837	3250	3642	3988	4367
	Re	3	7	13	15	25	50	50	40	67	26	50
Dre	Ads	231	450	790	975	1103	1366	1421	1550	1566	1766	1817
	Re	2	22	13	NR	NR	33	NR	NR	NR	50	17

Ads = Adsorbed zinc ($\mu g\ g^{-1}$) after 18 hours shaking for adsorption
Re = Recovered zinc (μg) from adsorbed zinc after dilution
NR = No desorption or recovery

desorption from the first 3 or 4 lower concentrations only. Midelney soil released a little amount from each concentration treatment with two times dilution by deionized water, while other soils showed no response to desorption of zinc from the higher concentrations. Dunlop soil indicated some response in mid part of the isotherm but no response in the first two low concentrations and in the last four concentrations. However it can be concluded that no soil was found that could release a significant amount of adsorbed zinc by 2 times dilution with water. All the soils perhaps adsorbed zinc by chemisorption, tightly bonded with adsorbing sites, that can only be released either by strong alkali metal salts or organic acids. There might be a little physisorption of the metal ions on to surfaces of clay due to Van der Waals forces but the water molecules probably had not approached with the force or energy sufficient to desorb the metal from the physisorbed metal portion. Chatterjee (1985) extracted 0.7-6.5% zinc of the amount retained by different soils with deionized water, while Sarkar et al. (1989) concluded that deionized water could not desorb appreciable amounts of zinc due to the process of chemisorption.

3.4.3 Desorption of zinc from the middle part of isotherm by x0, x2, x5, x10 dilution with deionized water

3.4.3.1 Method

In this experiment the middle part of the isotherm i.e; 40, 50, 60, 70, and 80 μg Zn cm^{-3} were taken and the

above 4 dilution points were studied in terms of desorption. A complete procedure has been given in Chapter 2 Section 2.5.4.

3.4.3.2 Results and Discussion

Zinc adsorption and desorption data have been represented in tables 3.5-3.9. It is evident from the tables 3.6 and 3.9 that Amlaird and Dreghorn soils have not shown any response towards desorption of zinc with respect to dilutions. The former soil remained unaffected while the later soil showed some further adsorption of zinc from the higher initial zinc concentration treatments. This extra adsorption of zinc could be due to the extra time given for desorption as earlier observed by many researchers (Brummer et al. 1988; Bakhsh, 1988).

Dunlop soil indicated a little response to zinc desorption with two times dilution only from the last four higher concentrations and showed 15-90 μgs zinc desorbed from the adsorbed amount. Caprington soil showed 50-400 μgs zinc recovery from the last three higher concentrations with respect to 2 times dilution and 50-100 μgs zinc with 10 times dilution.

The Midelney was the only soil which showed positive response to all dilutions in all concentrations. It is obvious from the table 3.8 that increasing the volume of dilution has increased the amount of zinc desorbed. Similarly more amount was desorbed as the concentration of added zinc was increased. This second observation was also noted in Caprington soil. The more desorption of zinc from

Table 3.5 Amount of Zn adsorbed on to Caprington soil ($\mu g\ g^{-1}$) from various initial concentration of zinc concentrations, and following differential dilution with deionized water

Dilution factor	Initial zinc concentration ($\mu g\ cm^{-3}$) (and amount of Zn adsorbed on to soil) ($\mu g\ g^{-1}$)				
	40	50	60	70	80
	1255	1487	1800	2100	2250
0	1262	1475	1800	2100	2250
x2	1250	1500	1750	1750	1850
	(5)	NR	(50)	(350)	(400)
x5	1300	1500	1850	2150	2200
	NR	NR	NR	NR	(50)
x10	1350	1500	1700	2050	2175
	NR	NR	(100)	(50)	(75)

The figures underlined (upper) represents the amount of zinc adsorbed $\mu g/g$ on to soil from different concentrations and the same are subjected for desorption by various dilutions with deionized water

2. The figures in parantheses denotes the amount desorbed in μgs with deionized water

3. NR means no recovery with the concerned dilution treatment or further adsorption is taking place.

Table 3.6 Amount of Zn adsorbed on to Amlaird soil ($\mu g\ g^{-1}$) from various initial concentrations of Zn, and following differential dilution with deionized water

Dilution factor	Initial Zn concentration ($\mu g\ cm^{-3}$) (and amount of Zn adsorbed on to soil) ($\mu g\ g^{-1}$)				
	40	50	60	70	80
	1480	1810	2175	2525	2675
0	1510	1830	2250	2425	2675
x2	1510	1800	2220	2550	2720
	NR	(10)	NR	NR	NR
x5	1575	1900	2300	2575	2850
	NR	NR	NR	NR	NR
x10	1505	1790	2295	2550	2800
	NR	(20)	NR	NR	NR

1. The figures underlined (upper) represents the amount of zinc adsorbed $\mu g/g$ on to soil from different concentrations and the same are subjected for desorption by various dilutions with deionized water
2. The figures in parantheses denotes the amount desorbed in μgs with deionized water
3. NR means no recovery with the concerned dilution treatment or further adsorption is taking place.

Table 3.7 Amount of Zn adsorbed on to Dunlop soil ($\mu g\ g^{-1}$) from various initial concentration concentrations of Zn, and following differential dilution with deionized water

Dilution factor	Initial Zn concentration ($\mu g\ cm^{-3}$) (and amount of Zn adsorbed on to soil) ($\mu g\ g^{-1}$)				
	40	50	60	70	80
	1675	2068	2331	2565	2837
0	1687	2050	2325	2565	2837
x2	1685	2031	2315	2560	2860
	NR	(37)	(16)	(90)	(15)
x5	1762	2113	2425	2737	2925
	NR	NR	NR	NR	NR
x10	1705	2100	2350	2700	2950
	NR	NR	NR	NR	NR

1. The figures underlined (upper) represents the amount of zinc adsorbed $\mu g\ g^{-1}$ on to soil from different concentrations and the same are subjected for desorption by various dilutions with deionized water
2. The figures in parantheses denotes the amount desorbed in μgs with deionized water
3. NR means no recovery with the concerned dilution treatment or further adsorption is taking place.

Table 3.8 Amount of Zn adsorbed on to Midelney soil ($\mu g\ g^{-1}$) from various initial concentrations of Zn, and following differential dilution with deionized water

Dilution factor	Initial Zn concentration ($\mu g\ cm^{-3}$) (and amount of Zn adsorbed on to soil) ($\mu g\ g^{-1}$)				
	40	50	60	70	80
	1675	2090	2587	2987	3362
0	1685	2092	2587	3012	3350
x2	1670 (5)	2080 (10)	2570 (17)	2970 (17)	3340 (22)
x5	1622 (53)	1990 (100)	2500 (87)	2900 (87)	3275 (87)
x10	1622 (53)	2000 (90)	2525 (62)	2870 (107)	3230 (132

1. The figures underlined (upper) represents the amount of zinc adsorbed $\mu g\ g^{-1}$ on to soil from different concentrations and the same are subjected for desorption by various dilutions with deionized water
2. The figures in parantheses denotes the amount desorbed in μgs with deionized water
3. NR means no recovery with the concerned dilution treatment or further adsorption is taking place.

Table 3.9 Amount of Zn adsorbed on to Dreghorn soil ($\mu g\ g^{-1}$) from various initial concentration of Zn and Zn and following differential dilution with deionized water.

Dilution factor	Initial Zn concentration ($\mu g\ cm^{-3}$) (and amount of Zn adsorbed on to soil) ($\mu g\ g^{-1}$).				
	40	50	60	70	80
	1206	1294	1425	1525	1612
0	1156	1325	1425	1562	1637
x2	1240	1440	1510	1725	1825
	NR	NR	NR	NR	NR
x5	1287	1550	1650	1750	1875
	NR	NR	NR	NR	(50)
x10	1450	1475	1675	1800	1925
	NR	NR	NR	NR	NR

1. The figures underlined (upper) represents the amount of zinc adsorbed $\mu g\ g^{-1}$ on to soil from different concentrations and the same are subjected for desorption by various dilutions with deionized water
2. The figures in parantheses denotes the amount desorbed in μgs with deionized water
3. NR means no recovery with the concerned dilution treatment or further adsorption is taking place.

the higher concentrations in these soils may be due to some unsatisfied zinc, loosely bonded with the adsorbent materials of soils with special reference to clay content.

3.5 Summary

First of all an appropriate shaking time for adsorption and desorption was concluded in the preliminary experiments. An 18 h shaking time was selected for both the adsorption and desorption studies after thoroughly studying different shaking times. Then the study was extended to find the appropriate concentrations of metals to be studied to know about the adsorption behaviour of metals in better way. Lastly the concentrations from 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 $\mu g\ cm^{-3}$, were selected for adsorption studies of metals. After that, different procedures were studied to have a convenient procedure for desorption of metals. For this purpose different experiments were run and finally the highest point of adsorption isotherm (100 $\mu g\ cm^{-3}$) was taken into study for desorption of metals. The dilution points were selected as 0, 10, 20, 30, 40, 50, 70, 100, and 120 cm3 and this study was fully applied in Chapter 4.

Chapter 4

Adsorption and desorption of metals on to soils in 0.1M $NaNO_3$ as a background electrolyte

4.1 Introduction

It is important to assess the effects of ionic strength and type of electrolyte when studying adsorption and desorption of trace metals on soils, because the background salt may complex metals and compete for adsorption sites. Certain anions complex metals to a greater extent than others (Lindsay 1979). There have been several investigations dealing with the effect of anion type on adsorption of zinc in soil. Shuman (1986) used .005, .01, .05 and 0.1M $NaNO_3$ to compare effects of ionic strengths on zinc adsorption by soils. He also used .01M Na_2SO_4, NaCl and $NaNO_3$ to compare the effect of different anions. Shuman observed that the higher was the ionic strength, the lesser was zinc adsorbed by soil. Adsorption of zinc by soil was greater from a SO_4^{-2} background salt than NO_3^- or Cl^-. Sodium salts of chloride, nitrate and sulphate were used at concentration of 0.05, 0.02, and 0.1M for zinc adsorption by soils by Elrashidi and O' Connor (1982). They found that neither ionic strength nor anion complex formation significantly affected zinc sorption. Pulford (1986) used potassium, sodium and calcium salts in forms of chloride and sulphate as background electrolyte for zinc adsorption by soil. He found only small differences in adsorption from sulphate

solution and considerable difference in the isotherms in the chloride system, depending on the cation of the supporting electrolyte. Sarkar et al.(1983) used 0.01M $CaCl_2$ as background electrolyte for adsorption-desorption behaviour of zinc in some representative soils of Andhra Pradesh, India. They found an increase in the amount of equilibrium concentration with increasing the amount of zinc in the system. They further stated that desorption indicated the absence of physical adsorption, existence of ion trapping mechanism, particularly in the high clay soil, appreciable change in sorption behaviour in the presence of eletrolytes and undersaturation of the soils with respect of $Zn(OH)_2$ or $ZnCO_3$.

Many research workers have used background electrolytes for copper as well as nickel adsorption-desorption behaviour in soils of different characteristics. Dhillon et al. (1981) investigated the adsorption of copper by alkaline soils, using 0.05M $CaCl_2$ as supporting electrolyte. They claimed that the adsorption data conformed to the competitive Langmuir adsorption equation and the adsorption capacities of soils were related to cation exchange capacity, clay content and $CaCO_3$ equivalent of soil. Assaad and Nielsen (1984) used 0.05M $CaCl_2$ as supporting electrolyte for copper adsorption on some Danish arable soils. They claimed that copper adsorption conformed to the linear form of the Langmuir isotherm, and considered copper adsorption as a pH-dependent process, increasing with soil pH and copper solution concentration. Padmanabham (1983) worked on

adsorption-desorption behaviour of copper(II) at the goethite-solution interface in the presence of 0.01M NaCl solution and revealed two types of adsorption site for copper(II) on the oxide surface, one of low bonding energy and the other of high bonding energy, corresponding with the 'readily desorbed' and 'less readily desorbed' fractions of copper(II) respectively. Jopony (1986) reported large hysteresis in the desorption isotherms of copper, showing irreversible retention of adsorbed copper on soil and sediment. He also concluded less desorption of adsorbed copper at low levels of copper adsorption compared with higher levels. He used 0.01M $CaCl_2$ as a supporting electrolyte and kept the equilibrion time five days.

Bansal (1985) studied the adsorption of nickel(II) on illite in presence of sodium and calcium nitrate and sulphate solutions. He concluded that equilibrium was attained in 3h at low concentration of sodium or calcium while within 8h at the highest sodium or calcium concentration. He further stated that adsorption of nickel increased up to the pH value 6.5 and then declined, and attributed this change to reduced competition from protons for active sites. He further stated that nickel adsorption was decreased with increasing ionic strength of ($NaNO_3$) or $Ca(NO_3)_2$. Tiller et al. (1984) used 10^{-2} M $Ca(NO_3)_2$ as an electrolyte to study the relative affinity of Cd, Ni, and Zn for different soil clay fractions and goethite. They concluded that in most cases the results confirm the established greater affinity of Zn, compared to Cd and Ni

for soil clays. Biddappa (1981) presented the magnitude of sorption in general in the order of Pb > Cu > Zn > Cd > Ni. The hysteresis of sorption and desorption by KNO_3 was well pronounced for both the metal ions and the soils. The desorption rate was greater than the fixation rate indicating the predominance of the chemisorption over physical processes.

The previous study in Chapter 3 on adsorption-desorption of Zn on soils in water background, has been extended to other two metals (Cu and Ni) along with Zn in this Chapter. But this time 0.1M $NaNO_3$ was used as supporting electrolyte, as water was not able to desorb zinc to appreciable amount due to domination of chemisorption. The electrolyte was used to provide better conditions for exchange reaction between solid and solution interface, and to reduce physisorption of metals. It is well known that sodium ions are a very good dispersing agent as well as good exchanger between solid and solution interface. It can readily adsorb on solid phases and can substitute with other metal ions present on solid or in solution. In soil adsorption-desorption processes are known to regulate the concentration of trace metal ions in solution and therefore trace metal adsorption-desorption study has great importance due to the increase in deficiency problems by industrial activity and land application of sewage sludge in some areas. The adsorption and desorption of trace metals by soils has importance in determining their availability to the plant

and their movement through the soil. Therefore the present study was carried out with the aim of;

(1) To know the adsorption-desorption behaviour of zinc, copper and nickel in soils in presence of sodium background electrolyte.

(2) To determine the adsorption capacity, bonding energy of soils, slope and correlation coeficients with the help of Langmuir and Freundlich isotherms

(3) To predict possible soil properties and characteristics responsible for adsorption and desorption.

(4) To see the effect of different dilution with 0.1M NaNO3 on the desorption of metals in terms of percent recovery (%R) from the adsorbed amount of metals on soils.

4.2 Adsorption behaviour of zinc, copper and nickel in soils

The same five soils studied in Chapter 3 were studied for their adsorption behaviour for zinc copper and nickel in 0.1M NaNO3 background instead of deionized water

4.2.1 Method

Similar method was used for the adsorption of these metals as used for adsorption of Zn in Chapter 3, but this time 0.1 M $NaNO_3$ was used as a background salt instead of water and in addition two other metals copper and nickel were also included in this work. Details of the procedure can be referred to in Chapter 2 Section 2.6.

4.2.2 Results and discussion

Adsorption isotherms obtained by plotting the amount of metal adsorbed versus concentration of metal in solution at equilibrium have been shown for five soils in the figures 4.1, 4.2, 4.3. They show the differences among the five soils for all the three metals , revealing the order of zinc adsorption as; Midelney > Amlaird ≥ Dunlop ≥ Caprington > Dreghorn. For copper the order of adsorption was Midelney > Amlaird ≥ Dunlop > Caprington > Dreghorn and for nickel it gave the order of adsorption as Midelney > Amlaird > Dunlop > Caprington > Dreghorn. The highest adsorption of all the three metals in Midelney soil and the lowest adsorption in Dreghorn soil may be due to the textures of these soils. The former soil is clayey and the later is sandy (Pulford, 1986; Bakhsh, 1988). Shukla and Mittal (1979) observed that more zinc was adsorbed by a loam soil than sandy soil, showing the effect of number of adsorption sites. Shuman (1975) and Bakhsh (1988) also found higher adsorption in clayey soils than sandy soils.

Dhillon (1981) supposed that the adsorption capacities of soils were related to cation exchange capacity , clay content and $CaCO_3$ equivalent of soil, while Jopony (1986) proposed that organic matter, Fe and Al oxides and clay minerals were possible mechanisms for strong retention of copper by soil and sediment constituents

Tiller (1984) revealed that there was evidence of greater relative affinity for nickel shown by clay fractions dominated by fine kaolinites when compared with

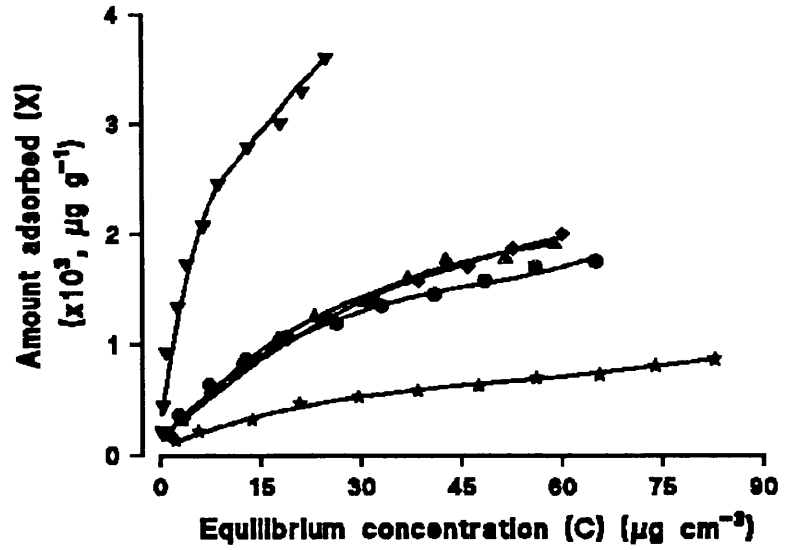


Fig. 4.1 Zn adsorption isotherms in the five soils in $NaNO_3$ background (●) Caprington (▲) Amlaird (◆) Dunlop (▼) Midelney (★) Dreghorn.

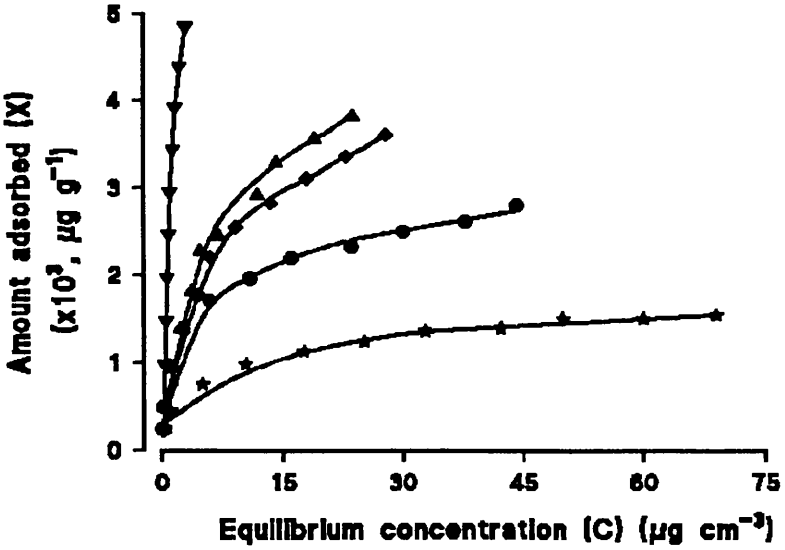


Fig. 4.2 Cu adsorption isotherms in the five soils in $NaNO_3$ background (●) Caprington (▲) Amlaird (◆) Dunlop (▼) Midelney (★) Dreghorn.

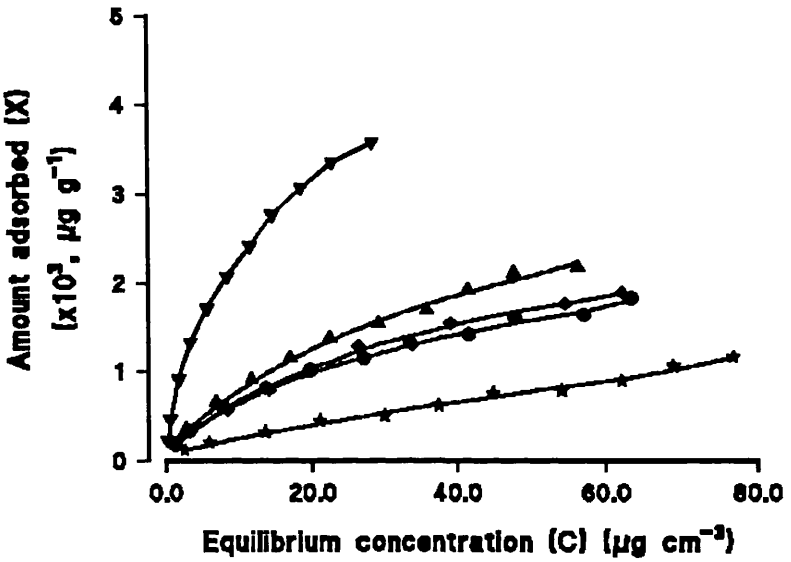


Fig. 4.3 Ni adsorption isotherms in the five soils in $NaNO_3$ background (●) Caprington (▲) Amisird (♦) Dunlop (▼) Mideiney (★) Dreghorn.

other clays.

It is evident from the figures 4.1-4.3 that Amlaird Dunlop and Caprington soils behaved almost similarly in respect of zinc and nickel adsorption, but Caprington soil showed a slight deviation from the similarity in adsorption of copper. The similarity in the behaviour of the former two soils with respect to the three metals adsorption may be due to their nearly similar physical and chemical properties, especially pH, clay content, organic matter and cation exchange capacity, which might have kept these soils similar in adsorption behaviour.

All the three metals showed initial fast adsorption in all soils, followed by slow and steady adsorption when concentration of the metal was being increased. Only in case of copper adsorption on Midelney soil, was this pattern not observed. This soil showed very fast adsorption from all the concentrations applied as treatments and about 97% copper was adsorbed from the highest concentration (100 μg Cu cm^{-3}) The reason for initial fast adsorption of metals at low concentration may be that first the most specific sites were occupied by the metal when the adsorbing sites were sufficient and metal ions were in low quantity. But at high metal concentration, sorption on sites of lower specificity could be expected since M^{+2} ion activity in solution would become high enough to compete effectively for the relatively specific sites. Singh and Abrol (1985) suggested that at low level of zinc application, sorption of zinc seemed to be a chemisorption whereas at high zinc

concentration, zinc could be held by a combination of both physisorption and chemisorption.

The affinity order of adsorption for zinc, copper and nickel was in order Cu > Zn ≥ Ni for all soils, except Dreghorn soil (figs. 4.4-4.8). In Dreghorn soil slightly more adsorption of nickel was observed in the upper part of concentrations, while in the lower part of concentrations it was almost similar to zinc adsorption. Almost similar sequence of adsorption was shown by Kinniburgh et al. (1976), who found the order of metal affinity for amorphous Fe hydroxides as;

Pb2+ > Cu2+ > Zn2+ > Ni2+ > Cd2+ Co2+ > Sr2+ > Mg2+.

With Al hydroxide he found a somewhat different sequence:

Cu2+ > Pb2+ > Zn2+ > Ni2+ > Co2+ Cd2 +> Mg2+ > Sr2+

Schnitzer (1966, 1967) revealed a typical affinity sequence of organic matter for metals (at pH5) as,

Cu > Ni > Pb > Co > Ca > Zn > Mn > Mg

But he further reported that these sequences are commonly inconsistent, dependent on the nature of the organic matter, the method used to measure metal bonding, and the pH at which bonding is measured. Biddappa (1981) presented the magnitude of sorption in general in the order of:

Pb > Cu > Zn > Cd > Ni.

Adsorption data of all the three metals were analysed according to the Langmuir adsorption equation which has been discussed in Section 1.4.1. The values of c/x versus c (metal in solution in $\mu g\ cm^{-3}$ were plotted

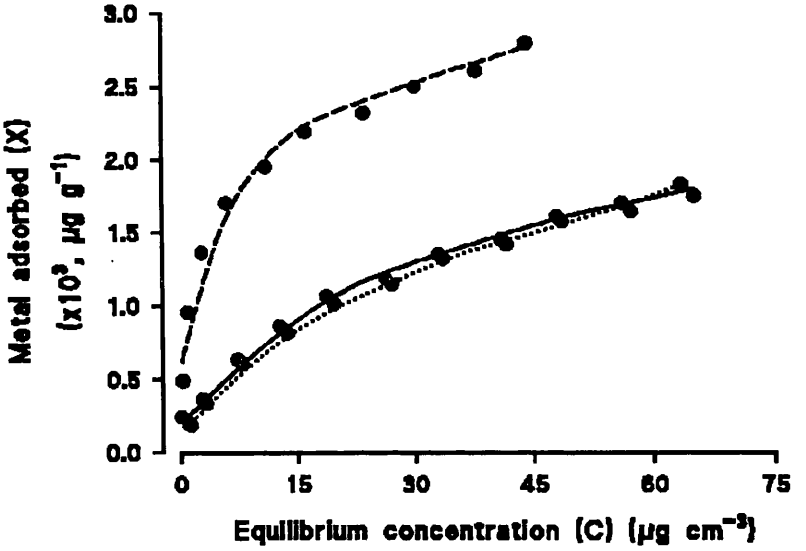


Fig. 4.4 Metals adsorption isotherms in the Caprington soil in $NaNO_3$ background (——) Zn (— —) Cu (·····) Ni.

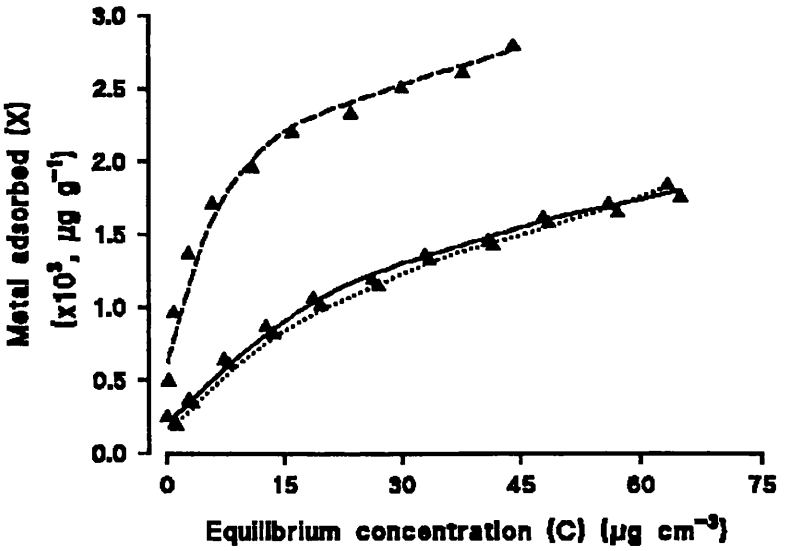


Fig. 4.5 Metals adsorption isotherms in the Amlaird soil in $NaNO_3$ background (——) Zn (— —) Cu (·····) Ni.

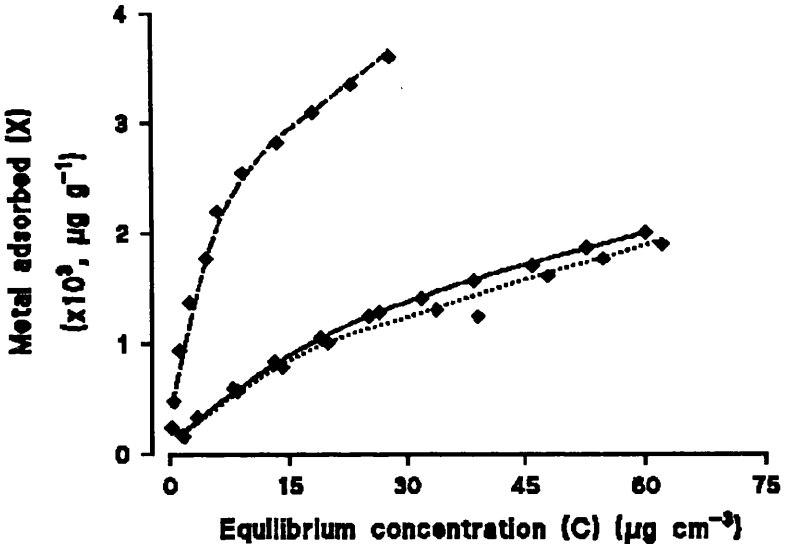


Fig. 4.6 Metals adsorption isotherms in the Dunlop soil in $NaNO_3$ background (——) Zn (— —) Cu (·····) Ni.

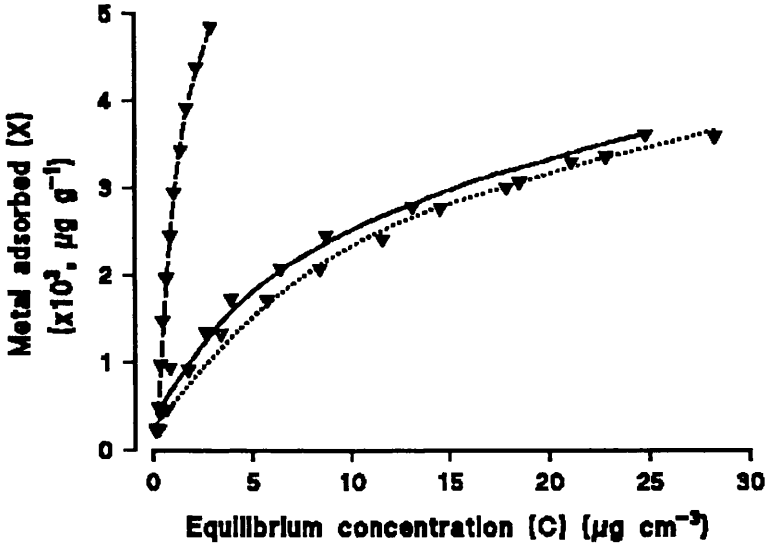


Fig. 4.7 Metals adsorption isotherms in the Mideiney soil in $NaNO_3$ background (——) Zn (——) Cu (·····) Ni.

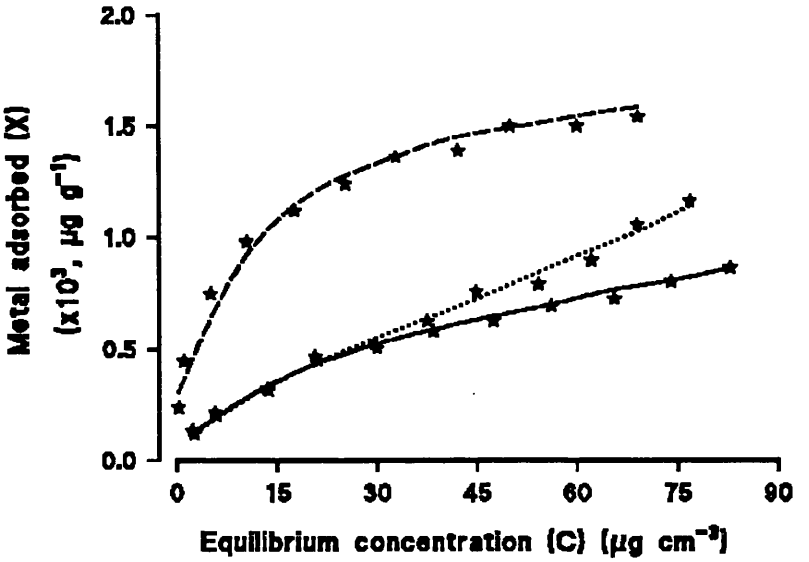


Fig. 4.8 Metals adsorption isotherms in the Dreghorn soil in $NaNO_3$ background (——) Zn (– – –) Cu (·····) Ni.

(figs. 4.9-4.23), to fit the data to Langmuir isotherm. The zinc adsorption data shows a good fit to this equation when one or two lower initial concentrations are neglected. (figs. 4.9-4.13) Harter and Baker (1977) suggested that this deviation at low concentration may be due to not considering the desorption of ions already on the surface. Veith and Sposito (1977) observed that precipitation and adsorption reactions give straight line plots when fitted to the Langmuir equation under certain experimental conditions. They suggested that if the measurements are made at very low equilibrium solution concentrations, the line for precipitation reactions bends upward and approaches infinite values. Chawla et.al. (1985) studied adsorption of zinc in some soils and reported that their data of zinc fitted well to the Langmuir isotherm.

The copper adsorption data presents a very good fit to Langmuir equation (figs. 4.14-4.19) with exception of Midelney soil (4.17). Midelney soil adsorbed nearly 97% of added copper from the highest concentration of 100 μg cm^{-3}. The first five initial concentrations gave a very little amount of Cu^{2+} in equilibrium solution which could not be accounted when data was analysed by Langmuir equation, and this is the reason these five points bent the line of adsorption upward, while the higher concentrations (50-100 μ g cm^{-3}) gave a straight line (fig 4.17) with R^2 (0.993). The other four soils indicate one kind of adsorption site as they produced a single linear lines when treated with Langmuir equation. Gerritse and Van Driel (1984) fitted Langmuir type-equation adequately

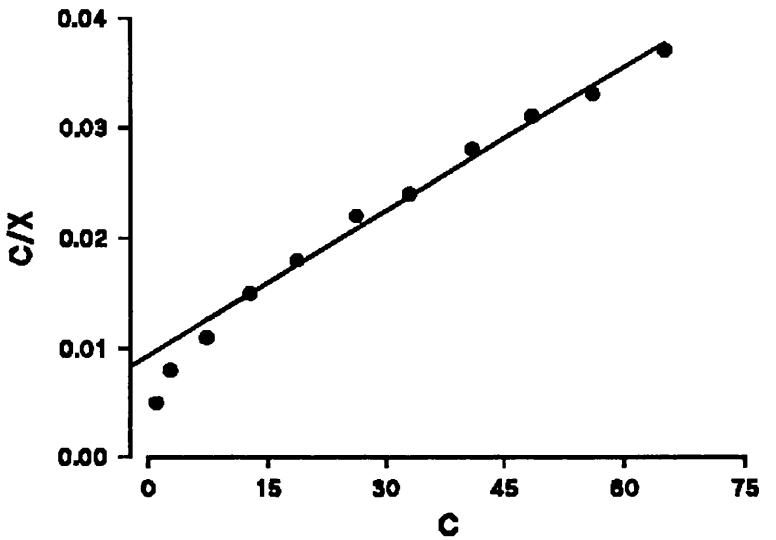


Fig. 4.9 Langmuir adsorption isotherm of Zn in Caprington soil.

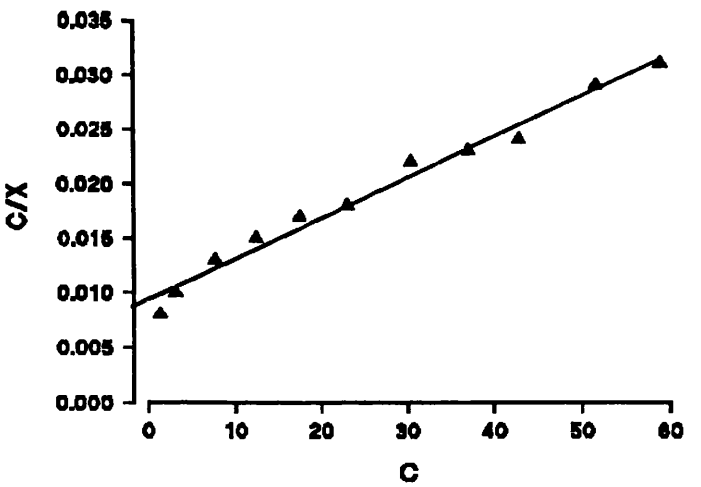


Fig. 4.10 Langmuir adsroption isotherm of Zn in Amlaird soil.

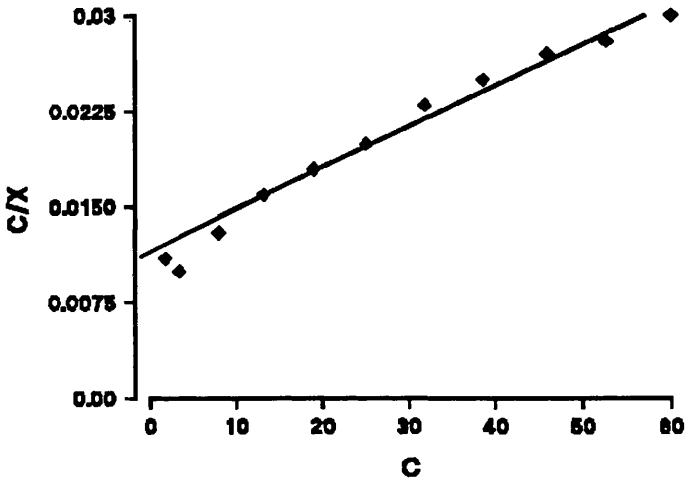


Fig. 4.11 Langmuir adsorption isotherm of Zn in Dunlop soil.

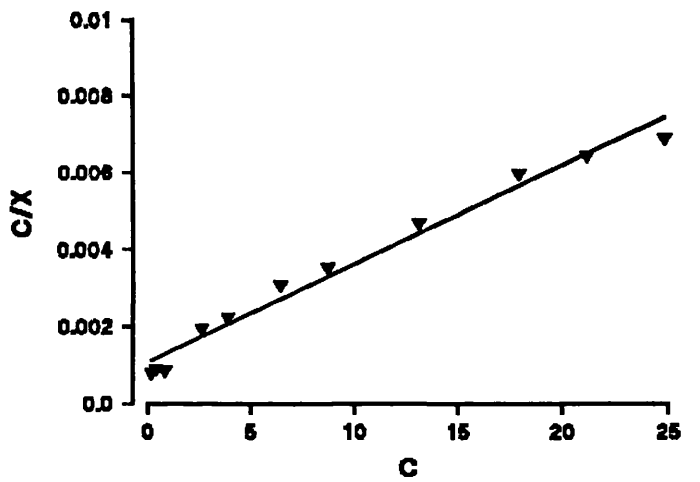


Fig. 4.12 Langmuir adsorption isotherm of Zn in Mideiney soil.

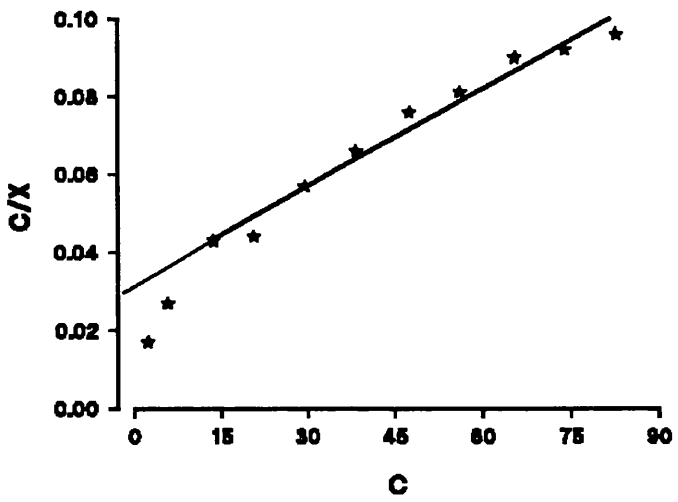


Fig. 4.13 Langmuir adsroption isotherm of Zn in Draghorn soil.

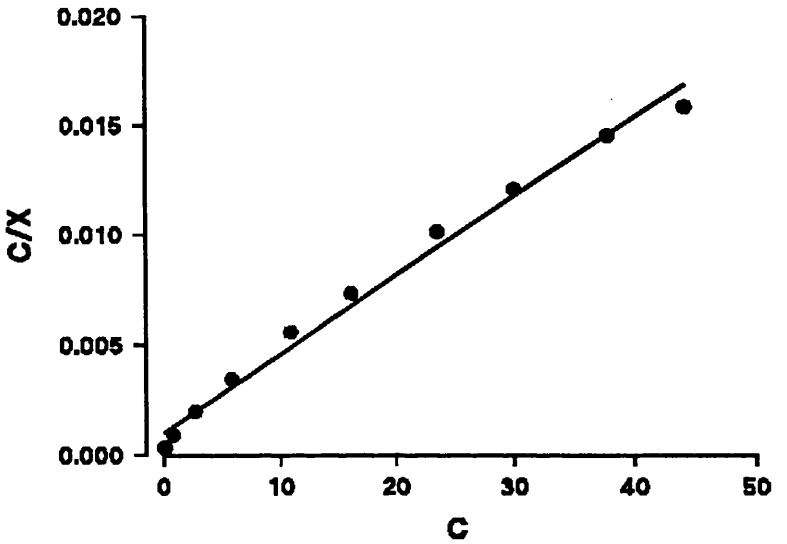


Fig. 4.14 Langmuir adsorption isotherm of Cu in Caprington soil.

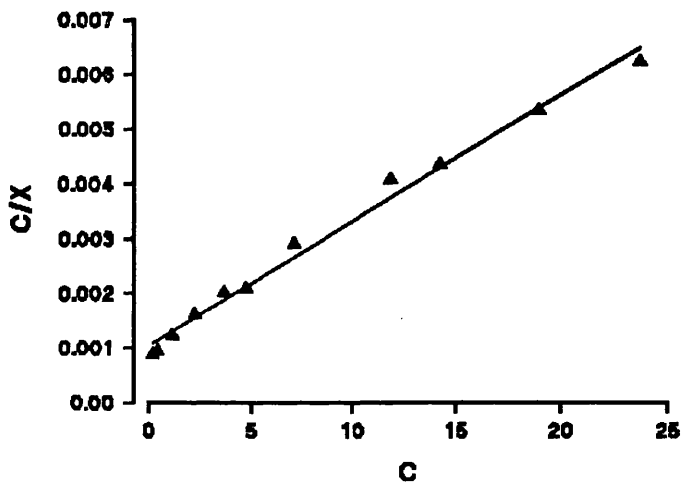


Fig. 4.15 Langmuir adsorption isotherm of Cu in Amlaird soil.

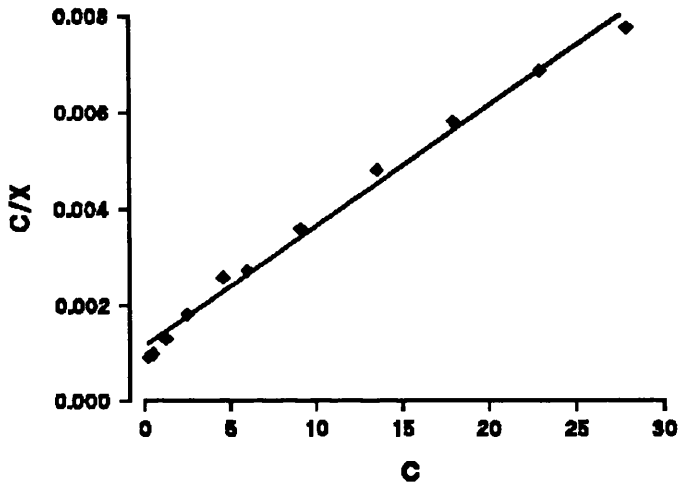


Fig. 4.18 Langmuir adsorption isotherm of Cu in Dunlop soil.

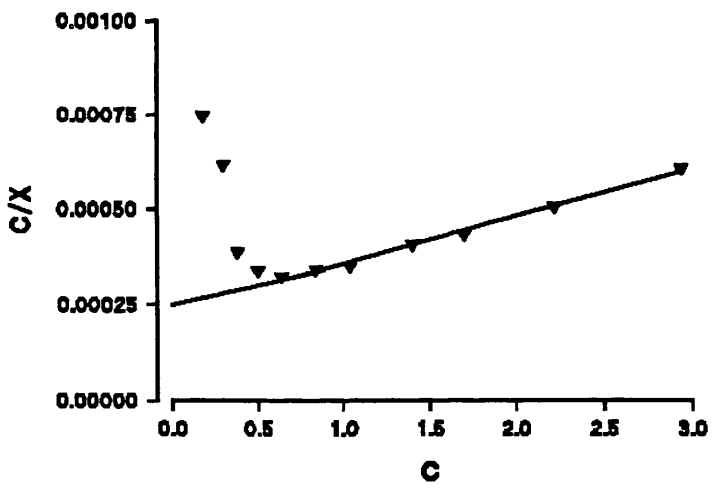


Fig. 4.17 Langmuir adsorption isotherm of Cu in Mideiney soil.

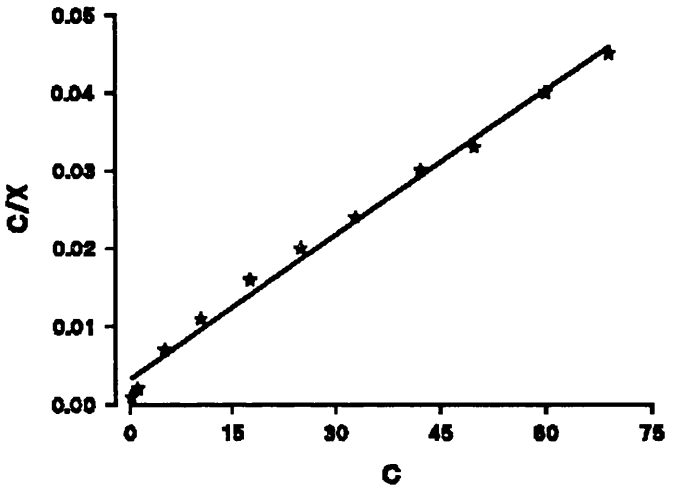


Fig. 4.18 Langmuir adsorption isotherm of Cu in Dreghorn soil.

to the adsorption data of copper for 33 soils and similarly Assaad and Nielsen (1984) showed that the copper adsorption data conformed to the linear form of Langmuir isotherm.

The nickel adsorption data produced good fit of Langmuir equation for all soils except Dreghorn (figs. 4.19-4.23), when one or two initial low concentration points were neglected as in the case of zinc adsorption data. It behaved similarly to zinc and probably the same causes could be given to this element behaviour as already discussed for zinc in the same section. Dreghorn soil gave very poor correlation (R^2 = 0.808) which does not conform to Langmuir equation. Due to very scattered points probably more than two isotherms could be drawn with a very few points. It is perhaps due to different adsorption sites with different reactions and with different retention capacity, however exact reason could not be drawn about such type of soil purely sandy in nature. Shuman (1975), Pulford (1986) and Bakhsh (1988) used this approach to their data of zinc adsorption by soils. They described their data by resolving the curves into two straight lines, as split isotherms. The existence of two linear lines and even more portions might indicate two types or even more types of adsorption or adsorption reaction in this particular soil.

The experimental data was also replotted according to Freundlich equation, presented by Bohn et al. (1985) in its linear form as below (see also section 1.4.1).

$$\log x/m = 1/n \log c + \log k$$

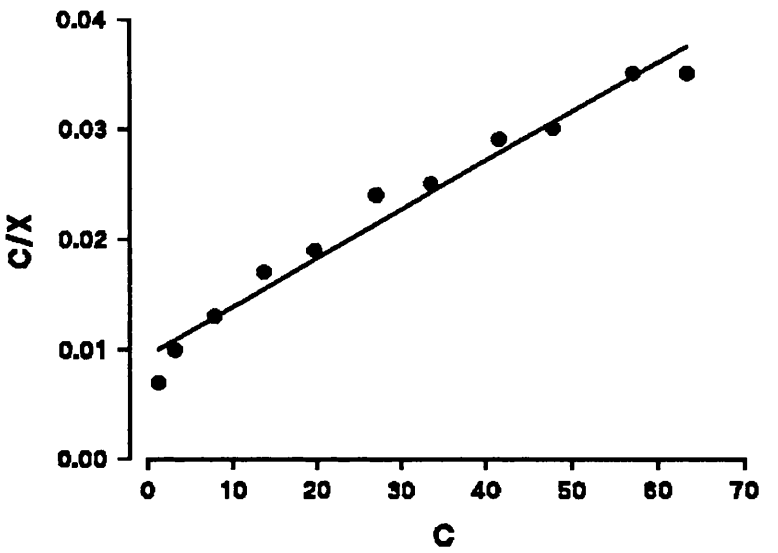


Fig. 4.19 Langmuir adsorption isotherm of Ni in Caprington soil.

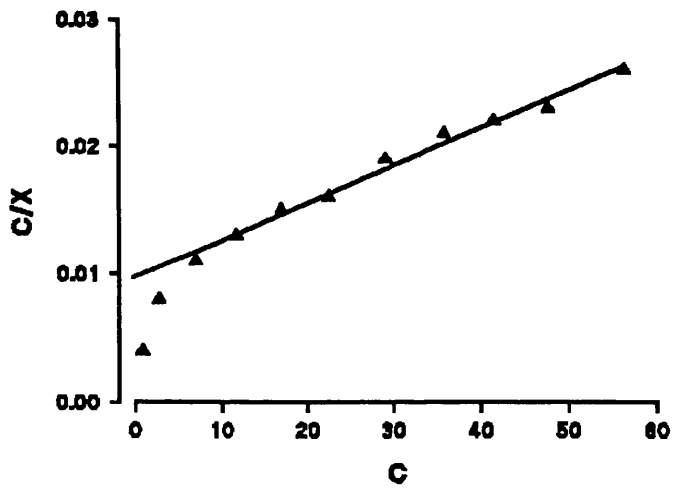


Fig. 4.20 Langmuir adsorption isotherm of Ni in Amlaird soil.

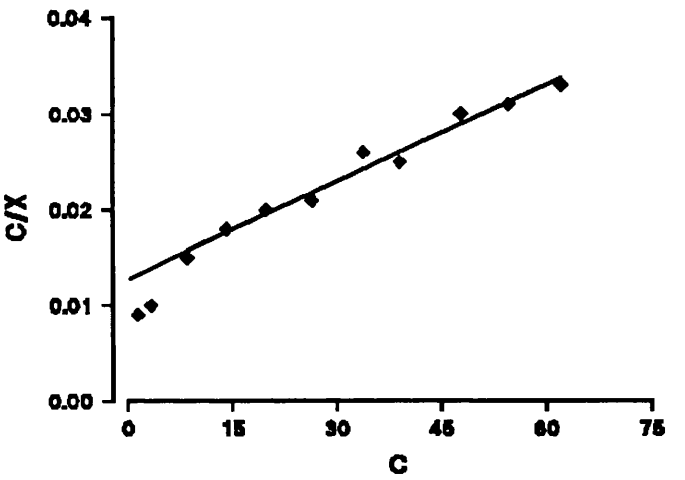


Fig. 4.21 Langmuir adsorption isotherm of Ni in Dunlop soil.

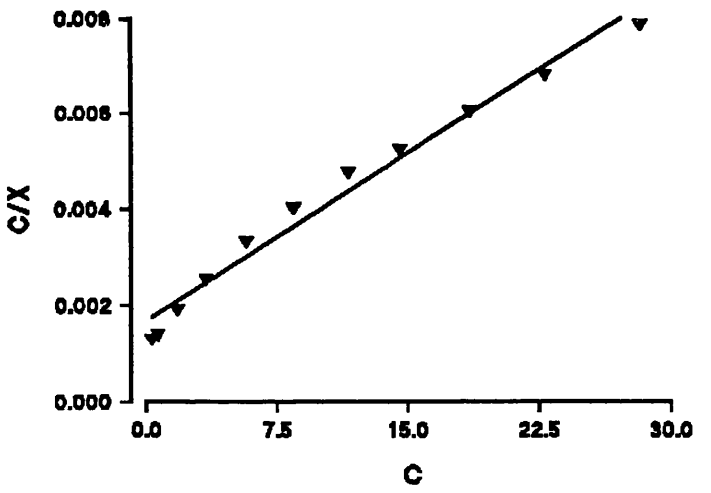


Fig. 4.22 Langmuir adsorption isotherm of Ni in Midelney soil.

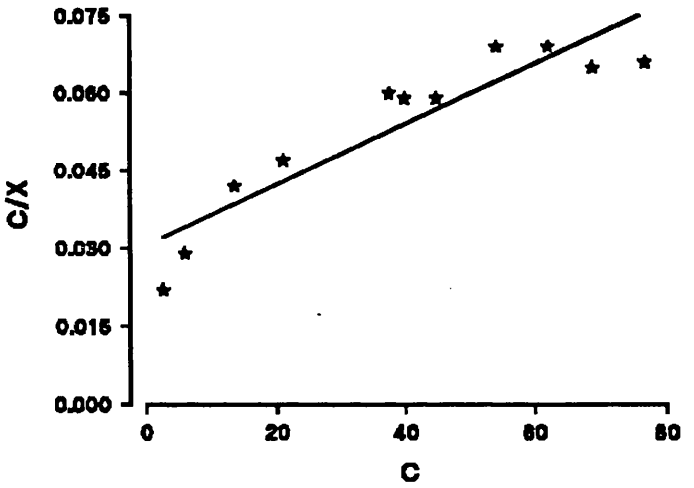


Fig. 4.23 Langmuir adsorption isotherm of Ni in Dreghorn soil.

All the soils except Midelney in case of copper conformed to the Freundlich equation when adsorption data of zinc, copper and nickel were analysed by this equation (figs. 4.24-4.38). Zinc and nickel adsorption data excellently fit to this equation as compared to copper, without any break point indicating only one kind of adsorption sites and the affinity between the adsorbate and adsorbent was dependent on the soil in question. Both metals adsorption though also conformed to Langmuir equation when one or two initial concentrations were neglected in the adorption, but not high correlation was observed compared to Freundlich equation, where R^2 was observed 0.99 or above (Tables 4.1 and 4.5). These results are well in conformity with those presented by Sarkar et al. (1989) who observed high degree of correlation between log c and log x while studying the adsorption and desorption of zinc in soils. They fitted the data excellently to Freundlich isotherm. Freundlich isotherms ran straight without any break point, which they presumed that only one kind of adsorption site is present. They further stated that a straight and parallel line was found when Langmuir equation was applied to the data and indicated a similar nature of adsorption reaction and the existence of only one kind of adsorption sites.

The copper adsorption data also conforms to Freundlich isotherm but not better than Langmuir isotherm. All soils reproduced a single straight lines except Midelney as already pointed out. This soil gave two straight line portions, which probably may be due to two

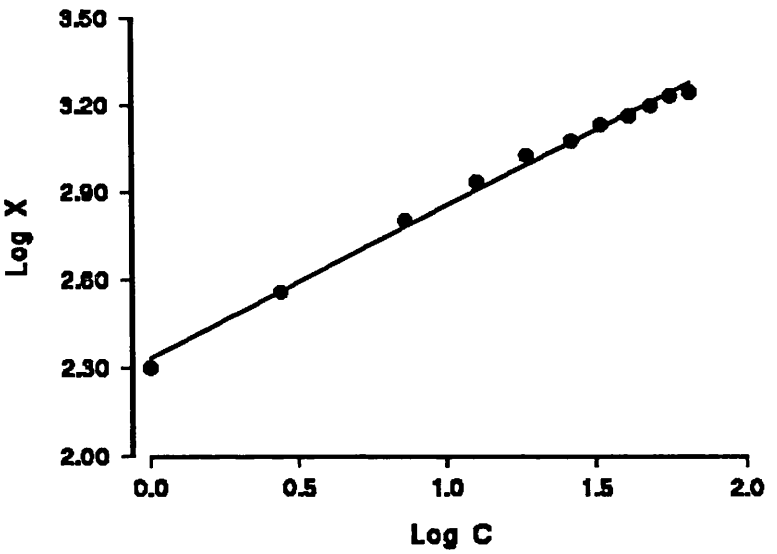


Fig. 4.24 Freundlich adsorption isotherm of Zn in Caprington soil.

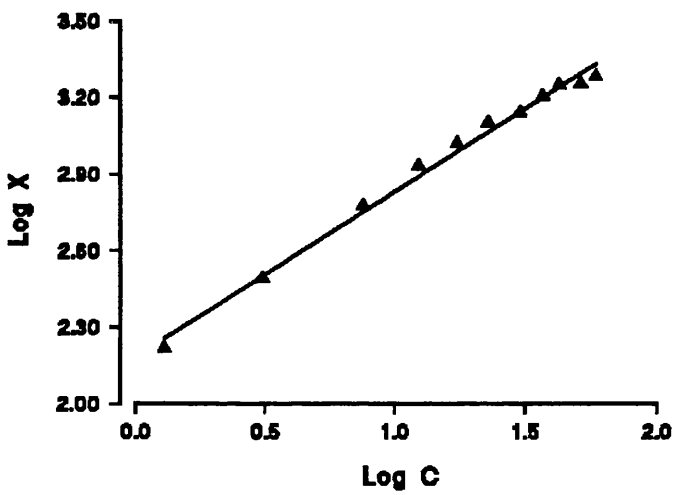


Fig. 4.25 Freundlich adsorption isotherm of Zn in Amlaird soil.

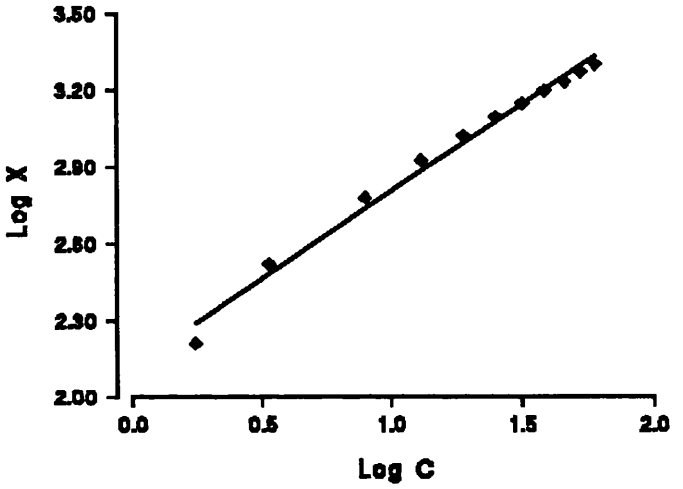


Fig. 4.26 Freundlich adsorption isotherm of Zn in Dunlop soil.

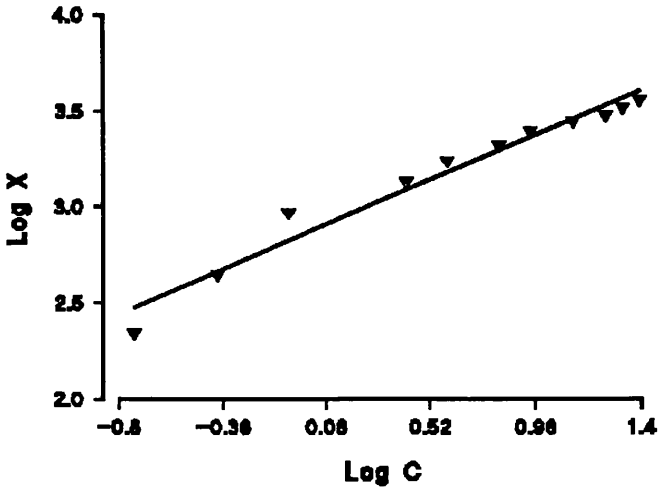


Fig. 4.27 Freundlich adsorption isotherm of Zn in Mideiney soil.

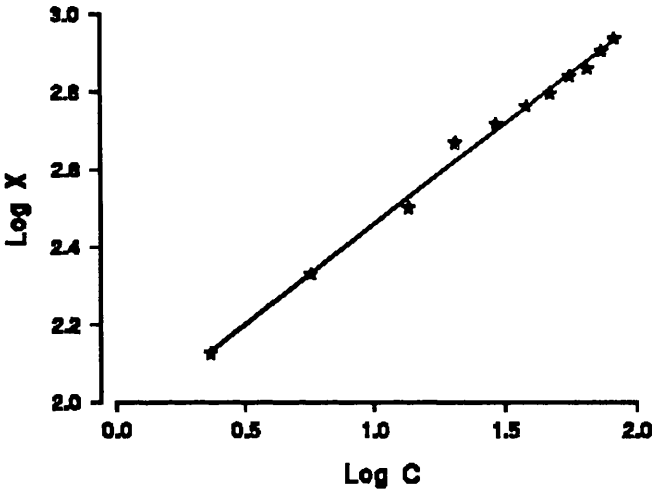


Fig. 4.28 Freundlich adsorption isotherm of Zn in Dreghorn soil.

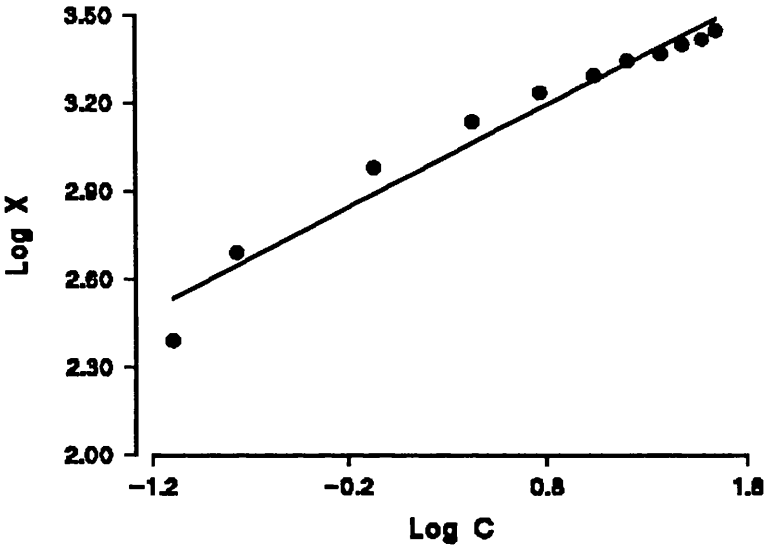


Fig. 4.29 Freundlich adsorption isotherm of Cu in Caprington soil.

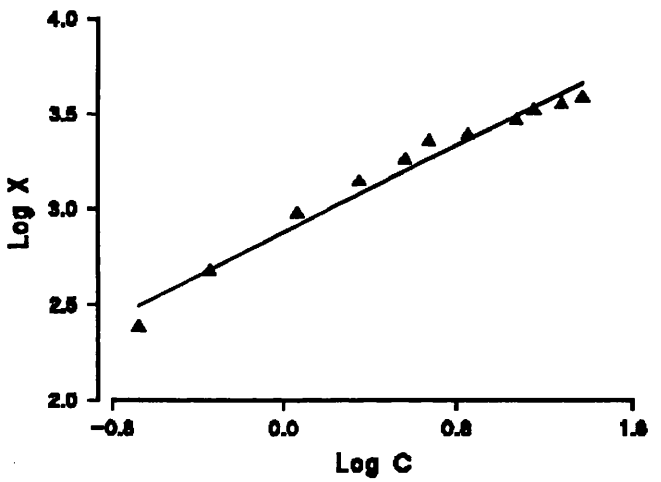


Fig. 4.30 Freundlich adsorption isotherm of Cu in Amlaird soil.

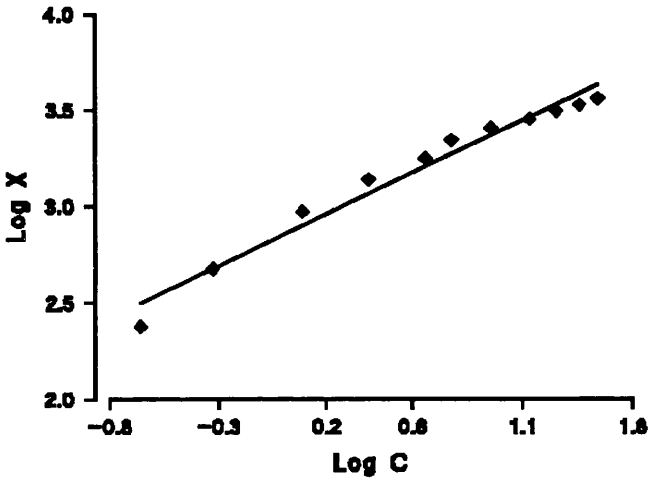


Fig. 4.31 Freundlich adsorption isotherm of Cu in Dunlop soil.

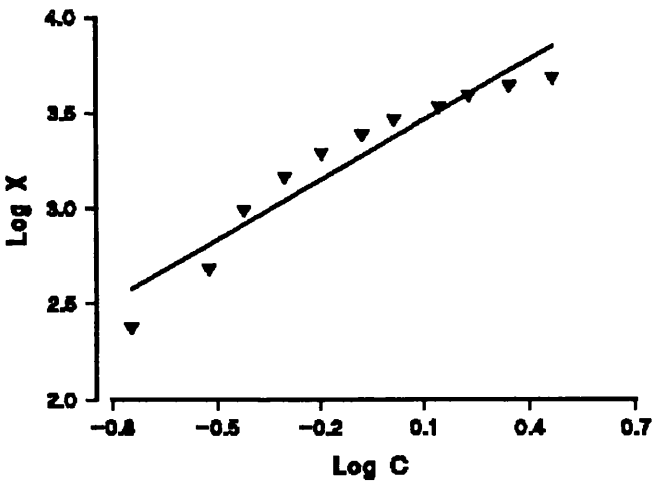


Fig. 4.32 Freundlich adsorption isotherm of Cu in Mideiney soil.

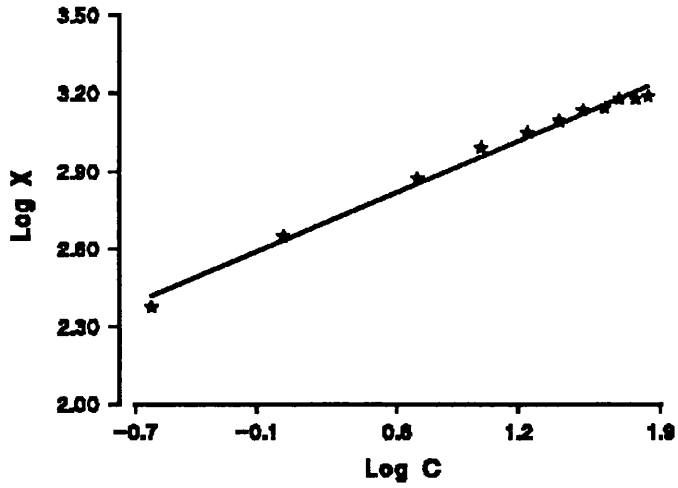


Fig. 4.33 Freundlich adsorption isotherm of Cu in Dreghorn soil.

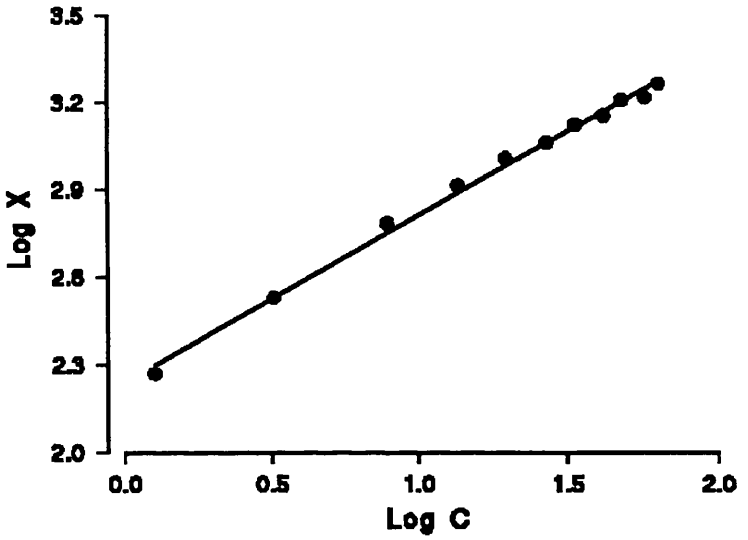


Fig. 4.34 Freundlich adsorption isotherm of Ni in Caprington soil.

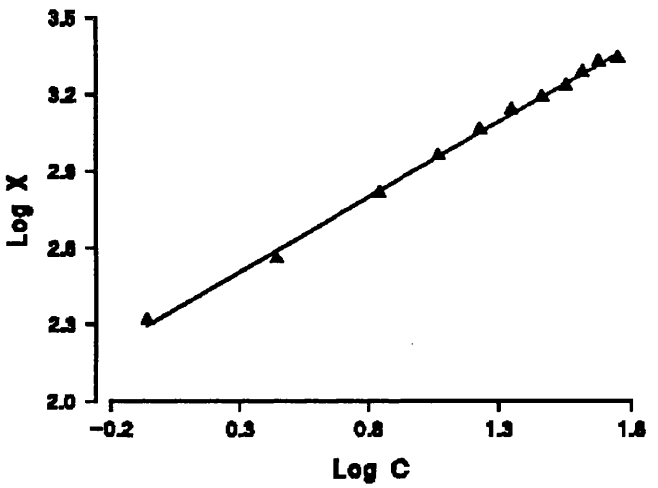


Fig. 4.35 Freundlich adsorption isotherm of Ni in Amlaird soil.

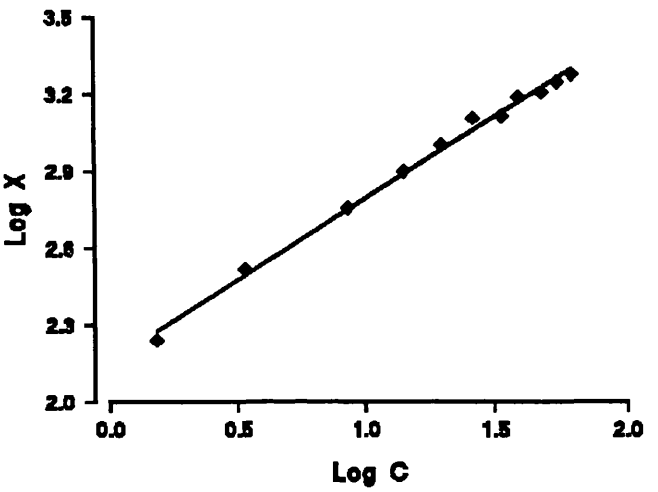


Fig. 4.36 Freundlich adsorption isotherm of Ni in Dunlop soil.

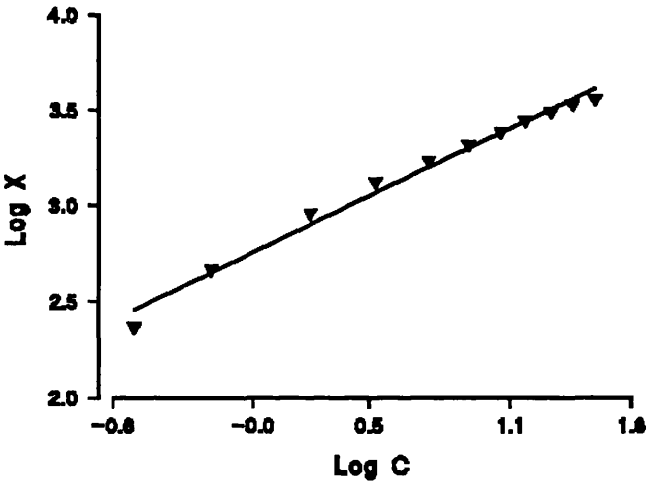


Fig. 4.37 Freundlich adsorption isotherm of Ni in Midelney soil.

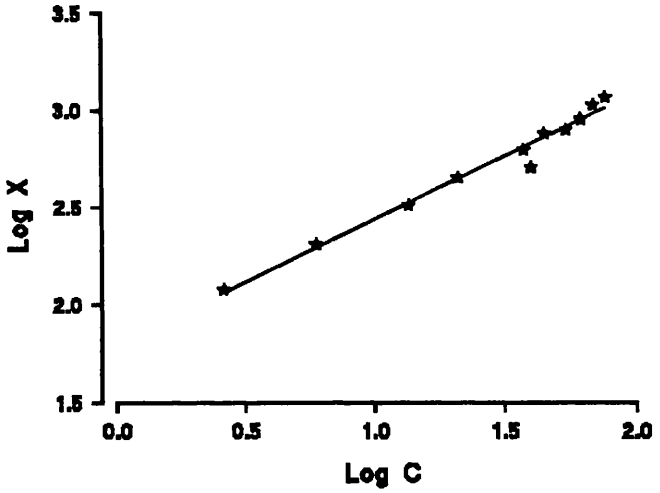


Fig. 4.38 Freundlich adsorption isotherm of Ni in Dreghorn soil.

different adsorption mechanisms on two separate adsorbents in the soil. This is well supported by the findings of Assaad and Nielsen (1985) who expressed their data of zinc adsorption in selected soils from Denmark, both by Langmuir and Freundlich equations. In one study soil they revealed 2 straight line parts by Freundlich equation and described that two adsorption mechanisms are taking place. Sanders (1980) reported that the adsorption of copper did not fit the Langmuir or Temkin equations very well, probably because of the heterogeneity of adsorption sites of the organic matter. They fitted double Langmuir and Freundlich equations almost equally well and overall Freundlich isotherm was preferred as it has only two parameters and the values of these are fairly stable to change in the range of copper concentration considered, or to doubling of the complexant concentration. The Sanders' findings are somewhat contradictary to this study, because his study on copper adsorption prefers Freundlich equation over Langmuir equation and the present study on the same issue relatively prefers Langmuir equation over Freundlich equation. Relan et al. (1980) conformed the adsorption data of zinc both to Freundlich and Langmuir equation, while Siddle and Kardos (1977) have found that the adsorption of copper, zinc and cadmium fitted Freundlich isotherms more closely than Langmuir isotherms.

Adsorption constants of zinc, copper and nickel for the five soils were calculated from Langmuir and Freundlich plots and are given in Tables 4.1, 4.3, 4.5. The zinc adsorption maxima in the five soils were in the

order Midelney > Dunlop > Amlaird > Caprington > Dreghorn (Table 4.1) and the bonding energy constants were in the sequence Midelney > Caprington > Amlaird > Dunlop ≥ Dreghorn. The copper adsorption maxima derived from Langmuir plot were in the order Midelney > Amlaird > Dunlop > Caprington > Dreghorn (Table 4.3) and the bonding energy constants gave the sequence as Midelney > Caprington > Amlaird ≥ Dunlop > Dreghorn. The nickel adsorption maxima revealed the order as Midelney > Amlaird > Dunlop > Caprington > Dreghorn (Table 4.5), while the bonding energy constants were in order Midelney > Caprington > Amlaird > Dunlop > Dreghorn. Generally the soils high in clay content and low in sand showed more adsorption capacities than soils with low clay content, and this was also the case with bonding energy constants. Shuman(1975) and Relan (1980) have proposed similar results.

Very good correlation coefficients were obtained for copper adsorption data as compared to zinc and nickel. All the soils gave R^2 nearly equal to 0.99 for copper adsorption data (Table 4.3). Zinc and nickel showed the range of R^2 from 0.97-0.99 and 0.81- 0.99 respectively for both the metals in the soils (Tables 4.1 and 4.5).

The slope, intercept and R^2 values for each soil and each element calculated from the Freundlich plots are also shown in the same Tables (4.1, 4.3, 4.5). Zinc and nickel shows an excellent R^2 i.e; 0.99 or above, while copper indicates R^2 range from 0.96-0.99 for all soils. These changes only indicate the heterogeneity of adsorption

TABLE 4.1 Zinc adsorption constants for five soils calculated from Langmuir and Freundlich plots in 0.1 M $NaNO_3$ background.

Soil	Langmuir plot			Freundlich plot		
	Adsorption maximum b, mg g^{-1}	Bonding energy k, l mg^{-1}	R^2	Slope	Intercept	R^2
Caprington	2.30	0.046	0.991	0.52	2.33	0.995
Amlaird	2.75	0.037	0.990	0.64	2.19	0.992
Dunlop	3.11	0.027	0.988	0.68	2.13	0.988
Midelney	3.93	0.233	0.980	0.65	2.19	0.992
Dreghorn	1.20	0.026	0.972	0.52	1.94	0.994

TABLE 4.2 Zinc desorption constants for five soils calculated from Langmuir and Freundlich plots in 0.1 M $NaNO_3$ background.

Soil	Langmuir plot			Freundlich plot		
	Adsorption maximum b mg g^{-1}	Bonding energy k lmg^{-1}	R^2	Slope	Intercept	R^2
1:Caprington A	1.90	0.190	99.5	0.24	2.85	82.7
2:Amlaird A	2.10	0.149	99.8	0.24	2.79	89.1
3:Dunlop A	2.14	0.248	99.6	0.20	2.98	80.9
4:Midelney A	3.82	0.660	99.9	0.14	3.37	92.5
5:Dreghorn A	0.94	0.125	98.0	0.20	2.56	74.3

TABLE 4.3 Copper adsorption constants for five soils calculated from Langmuir and Freundlich plots in 0.1 M $NaNO_3$ background.

Soil	Langmuir plot			Freundlich plot		
	Adsorption maximum b, $mg\ g^{-1}$	Bonding energy k, $l mg^{-1}$	R^2	Slope	Intercept	R^2
Caprington	2.79	0.373	0.989	0.35	2.91	0.962
Amlaird	4.38	0.218	0.990	0.57	2.88	0.971
Dunlop	4.02	0.217	0.991	0.54	2.85	0.970
Midelney	8.10	0.526	0.993	0.54	3.45	0.981
Dreghorn	1.62	0.193	0.992	0.33	2.62	0.990

TABLE 4.4 Copper desorption constants for five plots soils calculated from Langmuir and Freundlich plots in 0.1 M $NaNO_3$ background.

Soil	Langmuir plot			Freundlich plot		
	Adsorption maximum b $mg\ g^{-1}$	Bonding energy k $l\ mg^{-1}$	R^2	Slope	Intercept	R^2
1:Caprington A	2.99	0.382	99.1	0.18	3.18	72.6
2:Amlaird A	4.00	1.366	99.9	0.11	3.46	86.0
3:Dunlop A	3.76	1.400	99.9	0.07	3.47	81.7
4:Midelney A	4.90	204.000	100.0	0.001	3.69	2.4
5:Dreghorn A	1.60	0.580	99.9	0.12	3.01	64.4

TABLE 4.5 Nickel adsorption constants for five soils calculated from Langmuir and Freundlich plots in 0.1 M $NaNO_3$ background.

Soil	Langmuir plot			Freundlich plot		
	Adsorption maximum b, mg g^{-1}	Bonding energy k, l mg^{-1}	R^2	Slope	Intercept	R^2
Caprington	2.26	0.047	0.967	0.57	2.24	0.996
Amlaird	3.42	0.030	0.982	0.59	2.33	0.998
Dunlop	2.98	0.026	0.979	0.63	2.16	0.995
Midelney	4.31	0.138	0.979	0.59	2.76	0.986
Dreghorn	1.74	0.018	0.808	0.65	1.79	0.992

TABLE 4.6 Nickel desorption constants for five soils calculated from Langmuir and Freundlich plots in 0.1 M $NaNO_3$ background.

Soil	Langmuir plot			Freundlich plot		
	Adsorption maximum b, mg g^{-1}	Bonding energy k, l mg^{-1}	R^2	Slope	Intercept	R^2
1:Caprington A	2.10	0.170	99.4	0.21	2.91	95.0
2:Amlaird A	2.49	0.126	99.5	0.31	2.83	93.3
3:Dunlop A	2.21	0.191	99.7	0.25	2.90	87.0
4:Midelney A	3.83	0.777	99.9	0.11	3.41	97.8
5:Dreghorn A	0.23	0.014	88.9	0.30	2.59	77.9

surfaces or different adsorption mechanisms, otherwise Freundlich constants have no meaning when compared to Langmuir because Freundlich isotherm does not provide constants for adsorption maxima of soils.

4.3 Desorption behaviour of zinc, copper and nickel in soils

A desorption study was done only for zinc in Chapter 3 in water background, but due to very complex formation of zinc with soil components and within the solution, no appreciable amount of zinc was recovered from the adsorbed zinc. In other words a minute quantity of the study metal was brought back to solution by differential dilution with deionized water. Chemisorption seemed to be dominant rather than physisorption when deionized water was used as a background. To overcome or reduce the physisorption 0.1M $NaNO_3$ was used as a background electrolyte for zinc desorption as well as for two other elements, copper and nickel, and this was meant to replace one metal from the adsorbed surfaces by another metal (alkali). In normal cases it is very difficult to replace di-valent cation metal from the adsorbed surfaces by mono-valent cation metal. However due to sodium high affinity towards negative sites of the soil, it can compete to accommodate itself on the negative sites of the clay or other fraction of the soil by pushing other metal ions. Upon diluting the system with NaNO3, the metal concentration in the solution phase is decreased and thus some adsorbed zinc is exchanged into the solution to maintain equilibrium

between solid-phase zinc and liquid-phase zinc. This type of study was carried out in the current section to know the desorption behaviour of the three metals noted before, in 0.1M NaNO3 background. The effect of differential dilution with 0.1M NaNO3 on the desorption of metals will be seen in the following section of results and discussion and the metals recovered will be expressed graphically as well as in terms of percentage for all five soils. A comparative desorption isotherm for zinc, copper and nickel for each soil will be shown also in the same section.

4.3.1 Method

A method for desorption study of zinc, copper and nickel has been given in detail in Chapter 2 Section 2.6.

4.3.2 Results and discussion

The dilution effect of 0.1M NaNO3 on the desorption of metals has been represented graphically for each soil and each metal in figs. 4.39-4.53. All the soils showed very good response to the desorption of zinc and nickel except Midelney soil. Though the desorption of zinc and nickel seemed low with a few lower dilution but very steady and as the dilution was increased, somewhat more metal was desorbed. In some soils saturation point was also observed after a few dilutions, beyond which no further amount of zinc or nickel was desorbed (see figs. 4.39, 4.40, 4.43, 4.51, 4.52, and 4.53). Both these metals behaved almost similarly in all five soils. All the

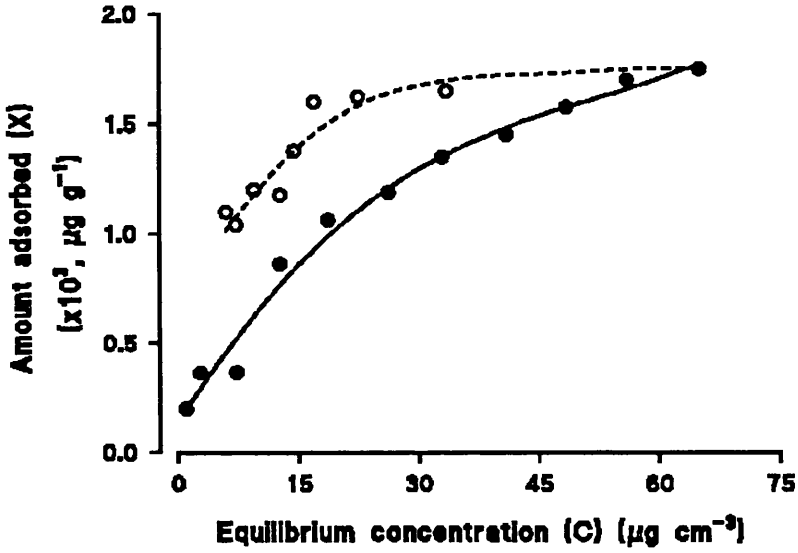


Fig 4.39 Adsorption and Desorption isotherms for Zinc in Caprington soil in $NaNO_3$ background. (——) Adsorption (- - -) Desorption

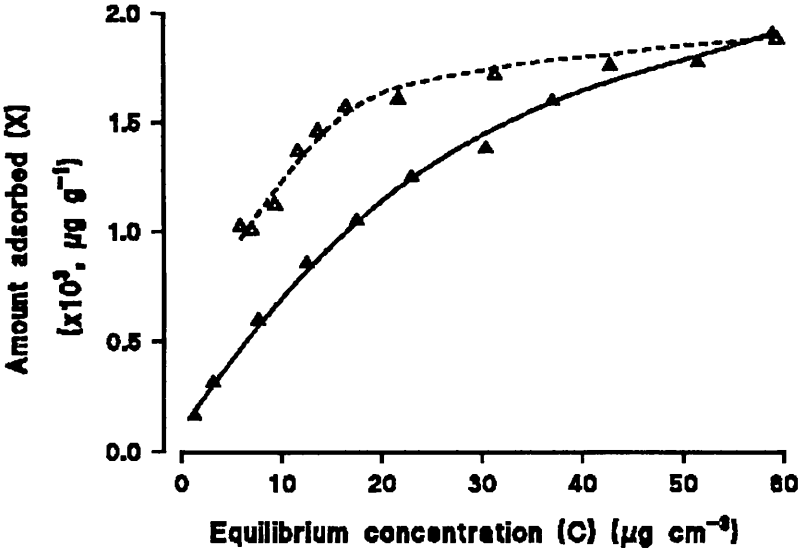


Fig 4.40 Adsorption and Desorption isotherms for Zinc in Amlaird soil in $NaNO_3$ background. (——) Adsorption (- - -) Desorption

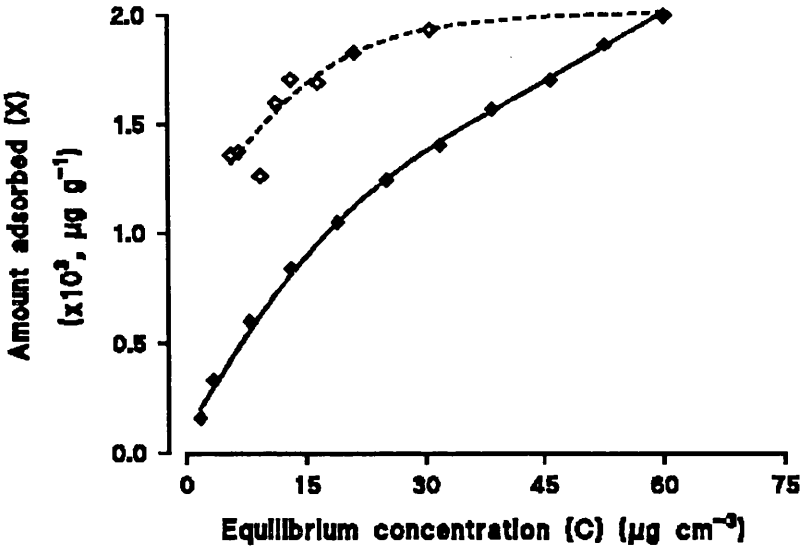


Fig 4.41 Adsorption and Desorption Isotherms for Zinc in Dunlop soil in $NaNO_3$ background. (——) Adsorption (---) Desorption

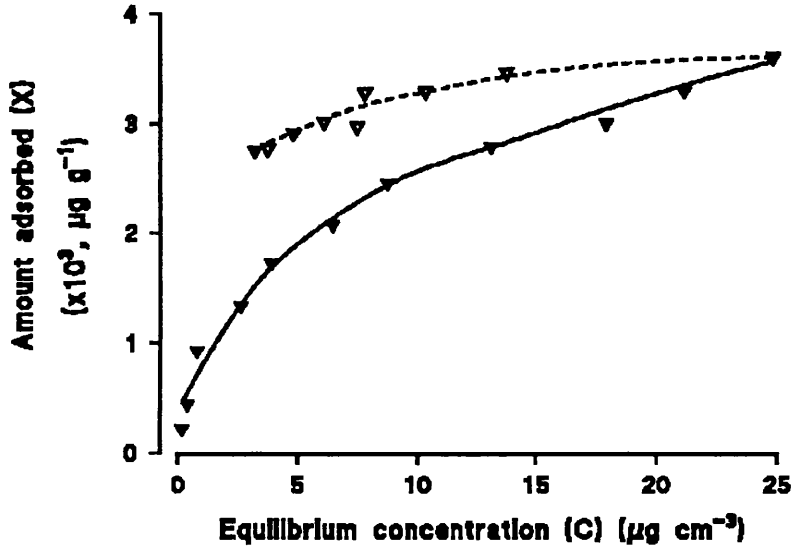


Fig 4.42 Adsorption and Desorption Isotherms for Zinc in Mideiney soil in $NaNO_3$ background. (——) Adsorption (---) Desorption

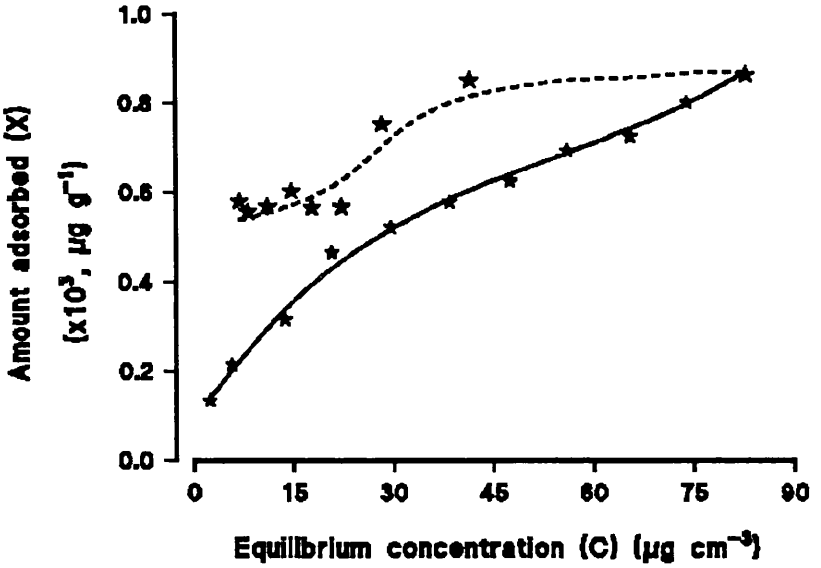


Fig 4.43 Adsorption and Desorption Isotherms for Zinc in Dreghorn soil in $NaNO_3$ background. (——) Adsorption (---) Desorption

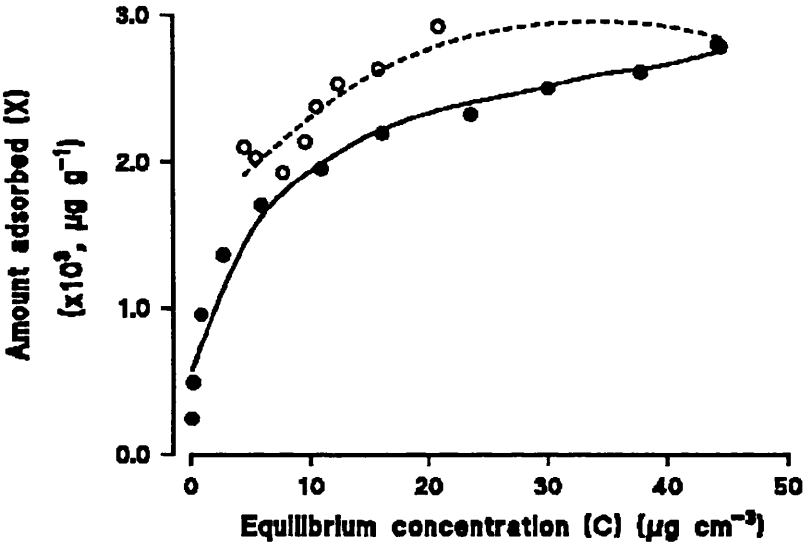


Fig 4.44 Adsorption and Desorption isotherms for Copper in Caprington soil in $NaNO_3$ background. (—) Adsorption (---) Desorption.

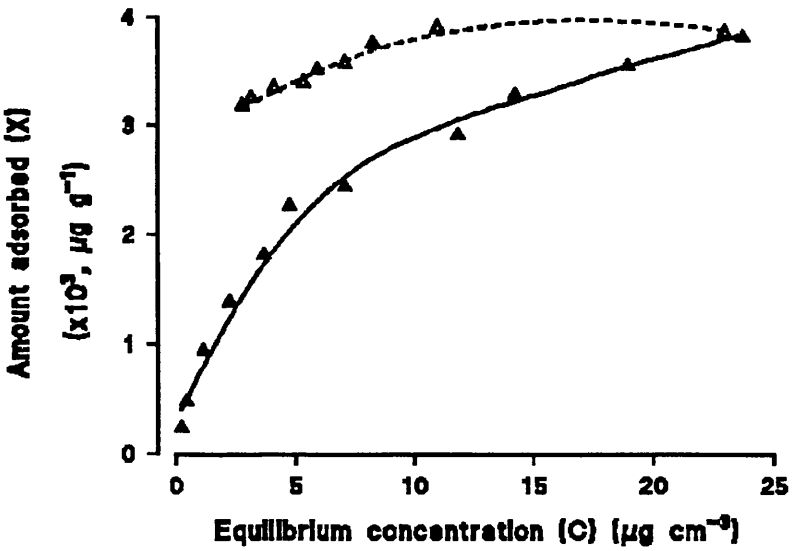


Fig 4.45 Adsorption and Desorption isotherms for Copper in Amlaird soil in $NaNO_3$ background. (—) Adsorption (---) Desorption.

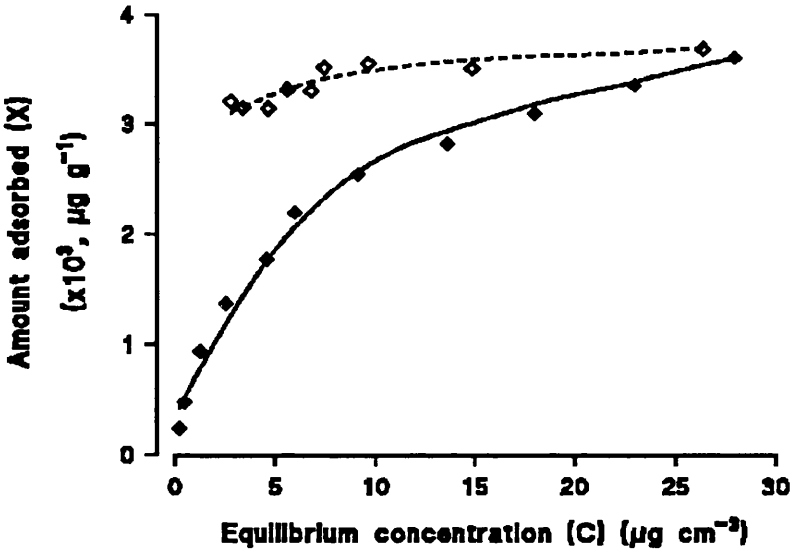


Fig 4.46 Adsorption and Desorption Isotherms for Copper in Dunlop soil in $NaNO_3$ background. (—) Adsorption (---) Desorption

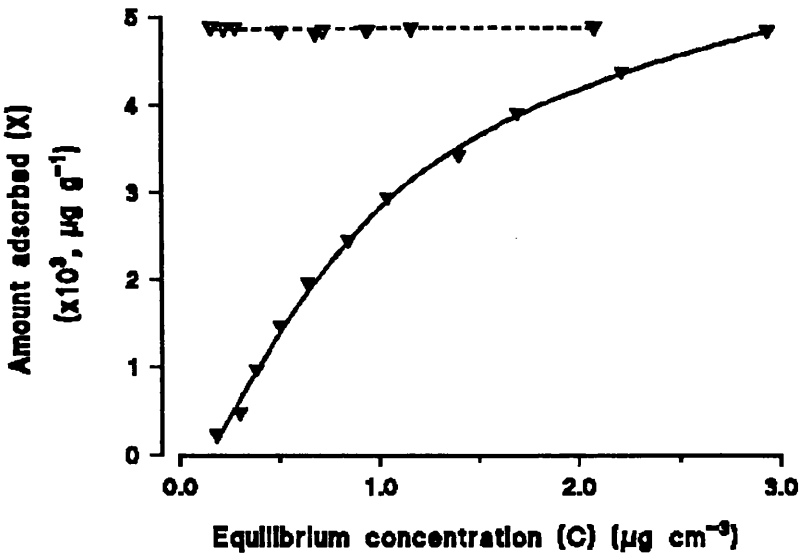


Fig 4.47 Adsorption and Desorption Isotherms for Copper in Midelney soil in $NaNO_3$ background. (—) Adsorption (---) Desorption

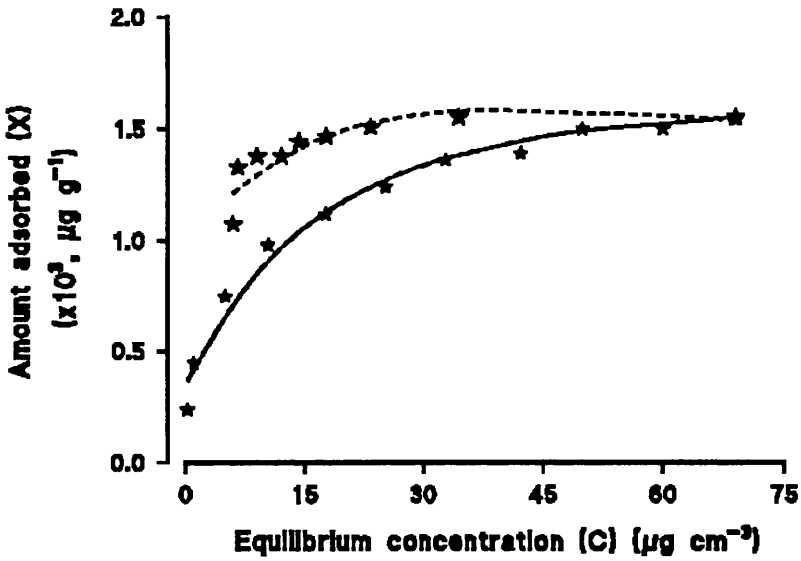


Fig 4.48 Adsorption and Desorption isotherms for Copper in Dreghorn soil in $NaNO_3$ background. (——) Adsorption (- - -) Desorption

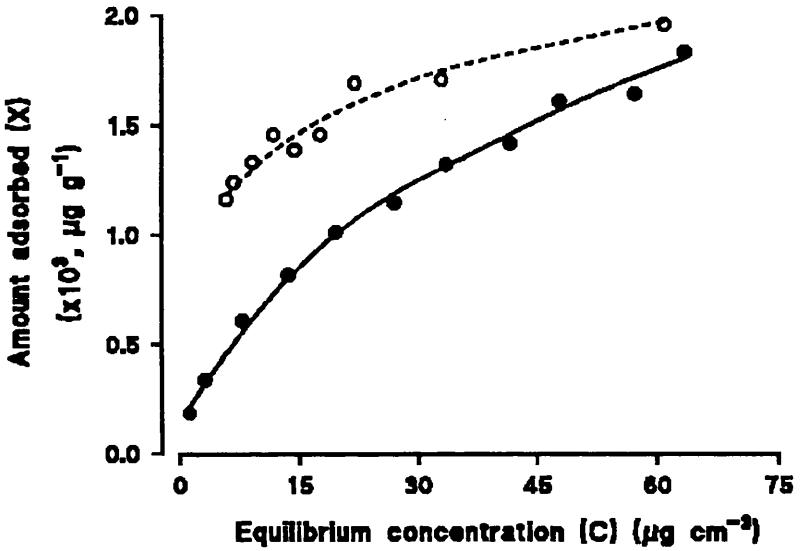


Fig 4.49 Adsorption and Desorption isotherms for Nickel in Caprington soil in $NaNO_3$ background. (—) Adsorption (---) Desorption

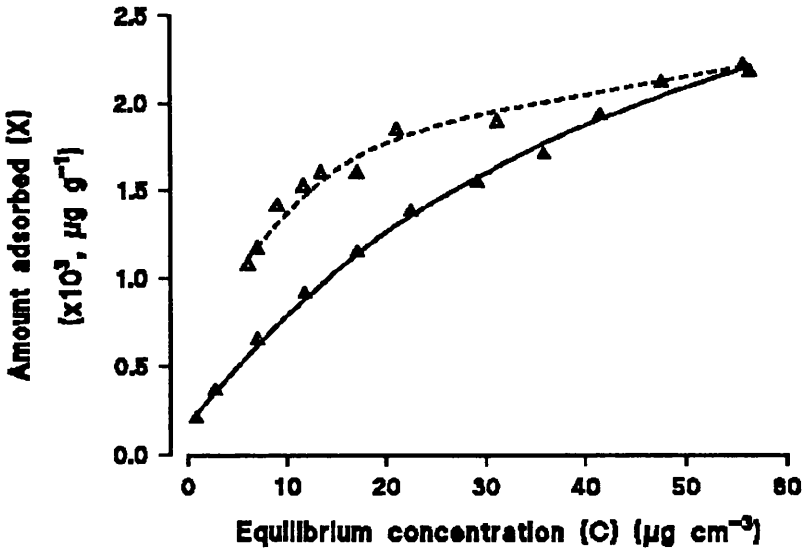


Fig 4.50 Adsorption and Desorption isotherms for Nickel in Amlaird soil in $NaNO_3$ background. (—) Adsorption (---) Desorption

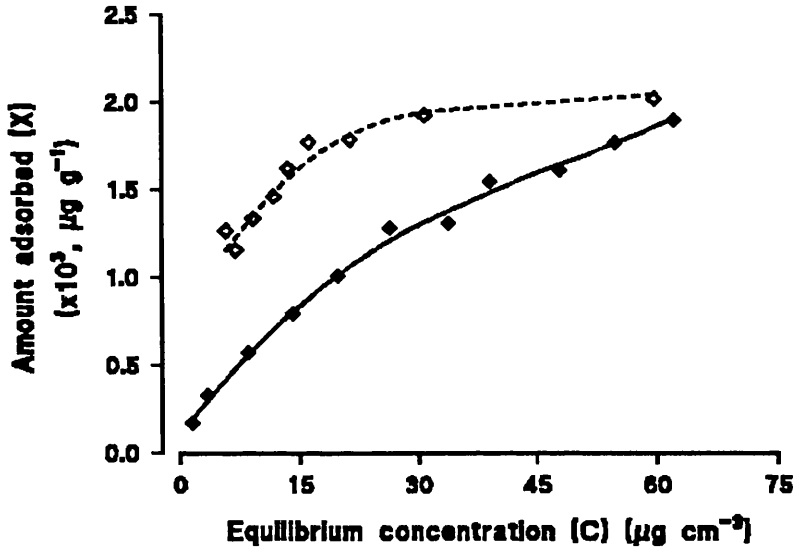


Fig 4.51 Adsorption and Desorption isotherms for Nickel in Dunlop soil in $NaNO_3$ background. (—) Adsorption (---) Desorption

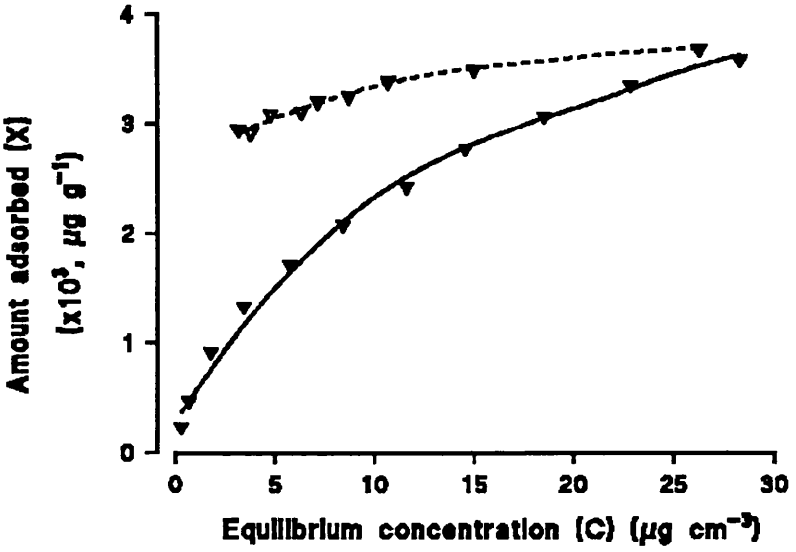


Fig 4.52 Adsorption and Desorption isotherms for Nickel in Mideiney soil in $NaNO_3$ background. (—) Adsorption (---) Desorption

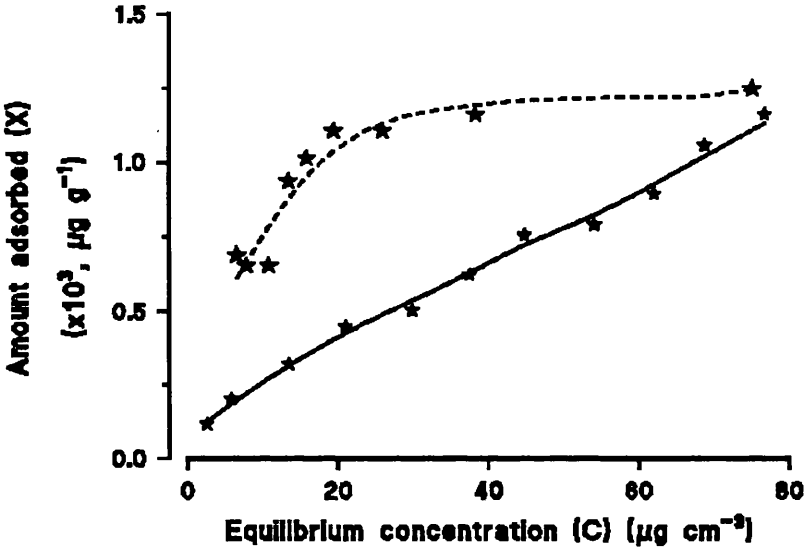


Fig 4.53 Adsorption and Desorption Isotherms for Nickel in Draghorn soil in $NaNO_3$ background. (——) Adsorption (---) Desorption

desorption graphs concerning zinc and nickel clearly show that after initial few dilutions the desorption curves seem to bend towards adsorption curves in all soils except Midelney. This means that after the initial dilutions when the system is diluted further an appreciable amount of metals are coming off the adsorbed surfaces into solution. In case of Midelney soil both the metals were very slowly desorbed, and therefore the line of desorption isotherm seems apart from the line of adsorption isotherm and is biased towards y-axis.

Figures 4.44-4.48 show the adsorption and desorption isotherms of copper in the five soils. The desorption trend for Amlaird, Dunlop and Dreghorn seems very similar, showing very slow desorption with respect to dilutions. Caprington soil indicates a better trend of desorption than all other soils and shows that as the dilution was increased more and more copper came off the adsorbate into the equilibrium solution. Up to 8-fold dilution it represents a steady desorption and then no further desorption is occuring with further dilution (fig 4.44). Probably the soluble or exchangeable part of adsorbed copper was desorbed by dilution up to this level and then further dilution has no access to the adsorbed copper which is perhaps strongly bonded with soil materials. No desorption at all happened in the Midelney soil (fig 4.47) and hence the line of desorption make a straight line along no dilution point.

Dilution with 0.1M $NaNO_3$ versus %Zn, Cu and Ni held on each soil was plotted, and are shown in figures 4.54-

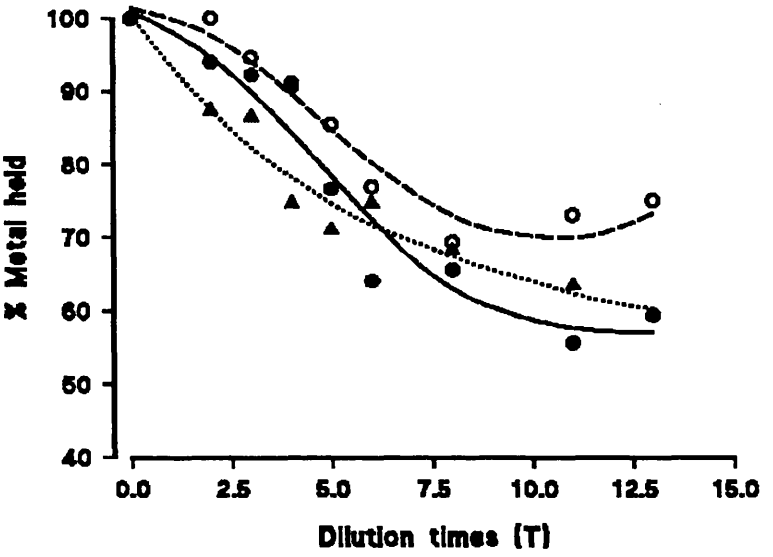


Fig. 4.54 Dilution factor versus % metal held in Caprington soil (●,——) Zn, (○,— —) Cu, (▲,·····) Ni.

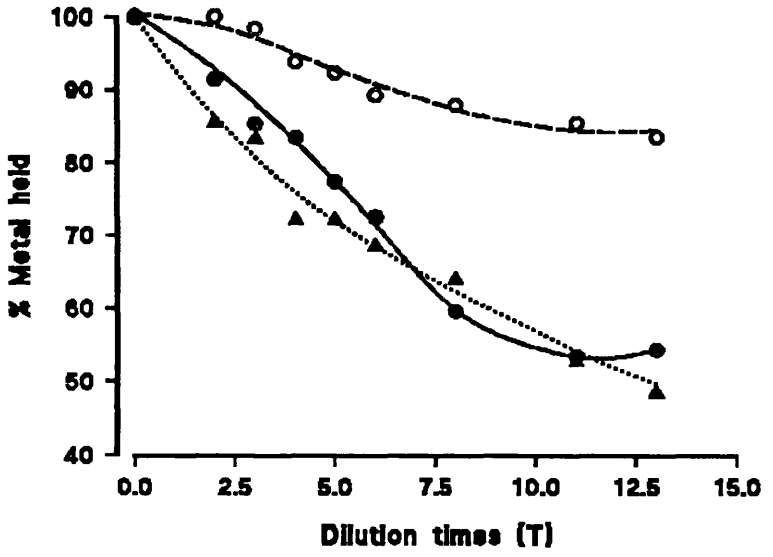


Fig. 4.55 Dilution factor versus % metal held in Amlaird soil (●,——) Zn, (○,— —) Cu, (▲,·····) Ni.

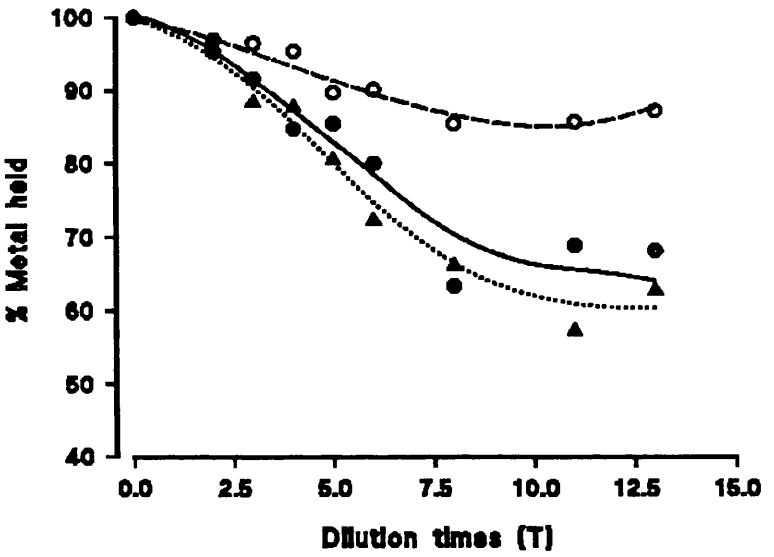


Fig. 4.56 Dilution factor versus % metal held in Dunlop soil (●,——) Zn, (○,——) Cu, (▲,·····) Ni.

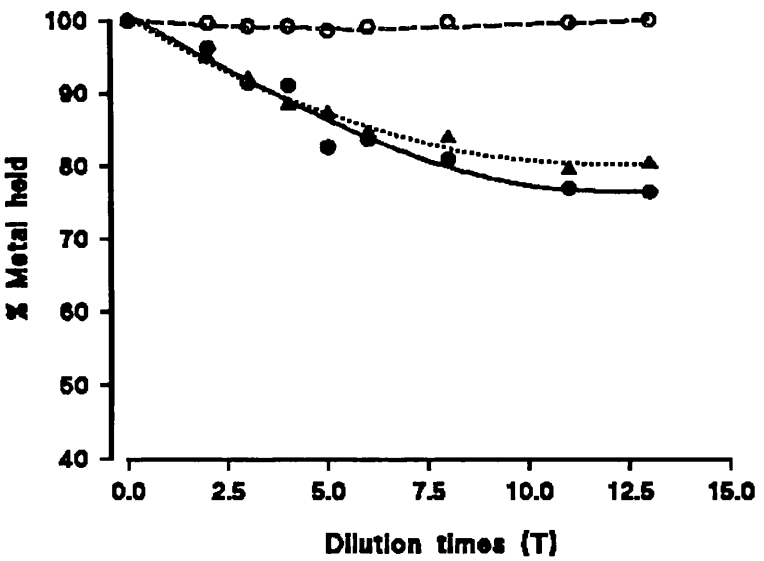


Fig. 4.57 Dilution factor versus % metal held in Mideiney soil (●,——) Zn, (○,——) Cu, (▲,·····) Ni.

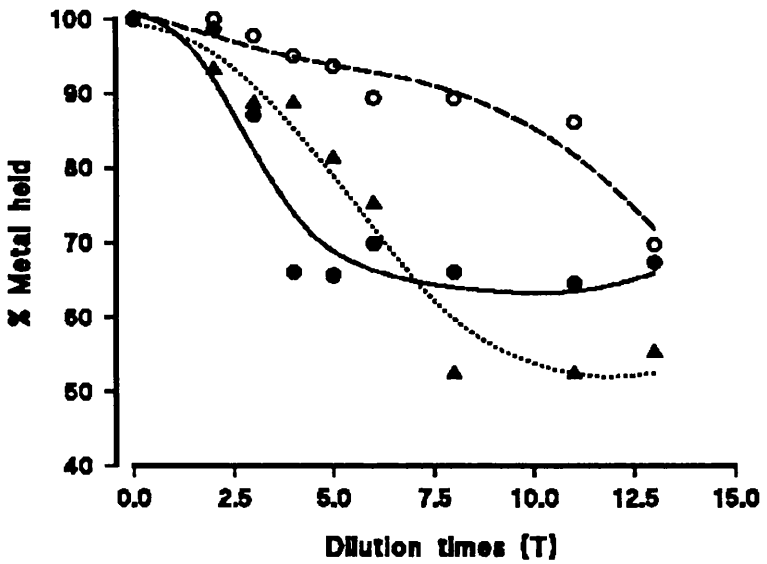


Fig. 4.58 Dilution factor versus % metal held in Dreghorn soil (●,——) Zn, (○,— —) Cu, (▲,·····) Ni.

4.58. They showed the desorption order almost in each soil as Zn ≃ Ni> Cu, revealing that copper is more reluctant to come off the adsorbed surfaces compared to zinc and nickel. Copper is very strongly adsorbed to organic matter which is rapidly adsorbed and more slowly desorbed (Bunzl et al. 1976), because copper needs greater heats of adsorption for the inner-sphere complexes formed between organic ligands and the copper itself, and on the other hand desorption necessarily requires that a large activation energy be overcome. All the soils except Caprington retained most of the adsorbed copper irreversible. Such suggestions were also given by Jopony (1986) while working on desorption of copper from soil and sediment. He observed that there was a large hysteresis in the desorption isotherms, showing irreversible retention of adsorbed copper. Zinc and nickel show a very good percentage recovered with dilution in every soil except Midelney. Midelney soil showed 20% and 22% recovery from adsorbed zinc and nickel respectively with different dilution by 0.1M $NaNO_3$ solution. All other soils showed the range of desorption from adsorbed zinc between 33-42%, and desorbed nickel from adsorbed nickel in the range of 38-51%. The major portion of sorbed metals were retained in the unextractable form, which overall accounted for more than 50% of the sorbed metals. These findings are well in conformity with those of Biddappa et al. (1981) who listed that more than 50% of the sorbed metals were retained in the unextractable form, while they were investigating adsorption, desorption, potential and

selective distribution of Cu, Zn, Cd, Pb and Ni in three typical soils of Japan under flooded condition. They gave the desorption order with respect to these metals as Ni > Zn, Cd > Cu, Pb.

Tables 4.7, 4.8 and 4.9 presents the summary of the effect of differential dilution on the desorption of metals from adorbed portions. It is evident from the Tables 4.7 and 4.9 that zinc and nickel desorption is almost similar and very small difference in amount desorbed is obvious in respect of differnt soils. All the soils except Dreghorn, desorbed almost equal amounts of zinc and nickel with differential dilution by 0.1M $NaNO_3$ solution. Dreghorn soil desorbed some what more nickel compared to zinc and the reason for it may be that nickel was not as strongly adsorbed by this soil as zinc. Copper showed different behaviour than zinc and nickel (Table 4.7) and also it showed a very little recovery with dilutions as compared to the other two metals. The order of desorption for zinc in this study for the soils were, Amlaird Caprington > Dreghorn Dunlop > Midelney. For nickel it presented the sequence as Amlaird > Dreghorn > Caprington Dunlop > Midelney and for copper it was in the order Caprington > Amlaird > Dreghorn Dunlop > Midelney. Amlaird soil showed the highest desorption of zinc and nickel while Midelney soil indicated the lowest desorption of these two metals. The former soil is the lowest in pH and the highest in organic matter content along with 52 meq / 100 gms of cation exchange capacity (Table 1.1), which is higher than

TABLE 4.7 Zn adsorption in percentage on the five soils and maximum % recovery after differential dilution with 0.1 M $NaNO_3$ solution, already treated with 10 cm^3 100 $\mu g\ cm^{-3}$ Zn solution.

Soil	Differential dilution and % Zn adsorption								Maximum % R
	No dilution %	2 T %	3 T %	4 T %	5 T %	6 T %	8 T %	11 T %	13 T %	R %
Cap A	100	94	92.2	90.6	76.6	64.1	65.6	55.6	59.4	42.5*
Aml A	100	91.4	85.3	83.4	77.4	72.5	59.6	53.4	54.3	44.2*
Dun A	100	96.9	91.6	84.7	85.4	80.0	63.3	68.8	68.1	33.3*
Mid A	100	96.2	91.4	91.1	82.6	83.7	80.9	76.9	76.4	22.0*
Dre A	100	98.7	87.1	66.0	65.5	69.9	66.0	64.5	67.3	33.5*

T = Times dilution.

%R = Maximum % Recovery.

* = Mean value calculated from the underlined values.

TABLE 4.8 Cu adsorption in percentage on the five soils and overall % recovery after differential dilution with 0.1 M $NaNO_3$ solution, already treated with 10 cm^3 100 μg cm^{-3} Cu solution.

Soil	Differential dilution (Times) and % Cu adsorbed									Max % R
	No dilution %	2T %	3T %	4T %	5T %	6T %	8T %	11T %	13T %	R %
Cap A	100	100	94.6	91.08	85.4	76.91	69.35	73.02	75.58	27.40*
Aml A	100	100	97.5	92.9	91.3	88.3	87.0	84.4	82.6	17.40
Dun A	100	95.4	96.5	95.4	89.7	90.1	85.4	85.6	87.1	14.00*
Mid A	100	99.75	99.24	99.18	98.65	99.06	99.84	99.65	100.0	0.57
Dre A	100	100	97.79	95.05	93.67	89.35	89.35	86.10	69.74	14.00

T = Times dilution.

%R = Maximum percent recovery.

* = Mean value calculated from the underlined values.

TABLE 4.9 Ni adsorption in percentage on the five soils and overall % recovery after differential dilution with 0.1 M $NaNO_3$ solution, already treated with 10 cm^3 100 μg cm^{-3} Nickel solution.

Soil	Differential dilution (Times) and % Ni adsorbed									Max % R
	No dilution %	2T %	3T %	4T %	5T %	6T %	8T %	11T %	13T %	R %
Cap A	100	87.3	86.5	74.6	71.0	74.6	68.2	63.4	59.5	40.5
Aml A	100	85.4	83.2	72.0	72.0	68.5	63.6	52.7	48.5	51.5
Dun A	100	95.4	88.4	87.7	80.4	72.3	66.1	57.3	62.6	38.0
Mid A	100	94.9	92.1	88.4	87.2	84.5	83.8	79.4	80.2	20.0
Dre A	100	93.2	88.7	88.7	81.4	75.1	52.4	52.4	55.2	46.7

T = Times dilution.

%R = Maximum percent recovery.

other soils. The later soil has the highest pH, second lowest in organic matter content and high content of clay. These characteristics of the soils have most probably contributed to the desorption of these metals in either way, whether more or less towards equilibrium concentration. Stevenson and Ardakani (1972) reported that in the organic matter, organic molecules are present, which are involved in forming soluble complexes; such as oxalic, citric, malic, tartaric and many other organic acids, aliphatic and aromatic, that are commonly in soil solution. Manley and Evans (1986), Pohlman and McColl, (1986) suggested that organic molecules with the capability to complex with metals can potentilly increase concentration of these metals in soil solution by dissolution at mineral surfaces. The desorption of these two metals in the rest of the three soils might be effected by their pH, organic matter or texture in either way and that might be one factor or two or even combination of many factors.

Copper showed the highest desorption in Caprington soil and the lowest in Midelney soil. The former soil has the lowest CEC among all the soils and also has the second highest organic matter content after Amlaird soil. Amlaird soil showed the second top position in the desorption order of copper. The latter soil (Midelney) showed only 0.57% copper recovery, from the adsorbed portion, which might not be counted as desorption and can be said that this soil did not give any response to dilution with 0.1M $NaNO_3$. The process seems in this soil to be chemisorption

and completely negating the physisorption. Possible mechanisms for irreversible retention of the adsorbed copper may be specific adsorption by soil organic matter and chemisorption at edges of clay minerals and precipitation in soil as hydroxides. Jopony (1986) reviewed that specific adsorption by soil organic matter and Fe and Al oxides are possible mechanisms for irreversible retention of the adsorbed copper. While chemisorption at edges of clay minerals and precipitation as hydroxides may also contribute to irreversible retention of the sorbed ions (Bruggenwert and Kamphorst, 1979); Jopony, 1986). The Caprington soil desorbed more copper compared to other soils may be due to its low cation exchange capacity. Sidle and Kardos (1977) had also the same approach and they supposed that higher organic matter content and cation exchange capacity probably contributed significantly to the binding copper.

Generally it was observed that a very little amount of copper was desorbed with dilution by 0.1M $NaNO_3$. Much of the adsorbed copper was not reversible due to very complex formation with soil components, especially organic matter and clay portion and were assumed responsible for irreversibility of this metal. It is obvious from the Table 4.8 that 14-27% Cu was recovered as a whole from the soils except Midelney which did not show any response to dilution in sense of desorption of copper. These results are almost similar to those reported by Hogg et. al. (1993). They recovered 2.4% to 8.3% copper from 98% initially adsorbed copper after 10 desorption periods.

Very appreciable amount of zinc and nickel was recovered with dilution by 0.1M $NaNO_3$ (Tables 4.7,4.9). It means that much of the portion of adsorbed metals were either in soluble or exchangeable sites, which upon dilution released the metals in solution. Geritse and VanDriel (1984) listed a range of exchangeable fractions about metals as 1-5% of total in the soils for Pb and about 10-50% for Cd, Zn and Cu.

When Langmuir equation was applied to the desorption data of study metals, all the soils according to this equation fit very well and produced single straight lines (figs. 4.59-4.73) except Dreghorn in case of nickel desorption (fig 4.73). This means that one kind of desorption reaction or desorption site is responsible for the release of these metals into solution. These specific sites might have some part of adsorbed metals in soluble or exchangeable fractions, which desorbed slowly with increasing dilution. Padmanabham (1983) also observed a single curve, when desorption was carried out at the pH of adsorption of zinc(II), e.g. at pH 5.5 in the presence of chloride or nitrate. It indicated a fixed amount of the 'less readily desorbed' fraction. The Dreghorn soil in case of nickel desorption did not fit to Langmuir equation and very poor correlation coefficient was observed. This may be due to high heterogeneity in this soil, showing more than one type of adsorption sites with different bonding energies which resulted uneven desorption. All the soils were also applied to the Freundlich equation to analyse the desorption data of the three metals according

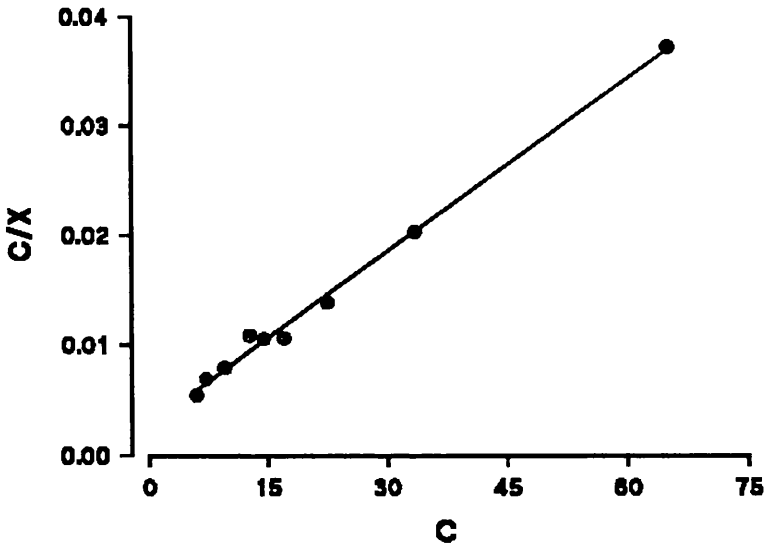


Fig 4.59 Langmuir isotherm for desorption of Zinc in Caprington soil in $NaNO_3$ background.

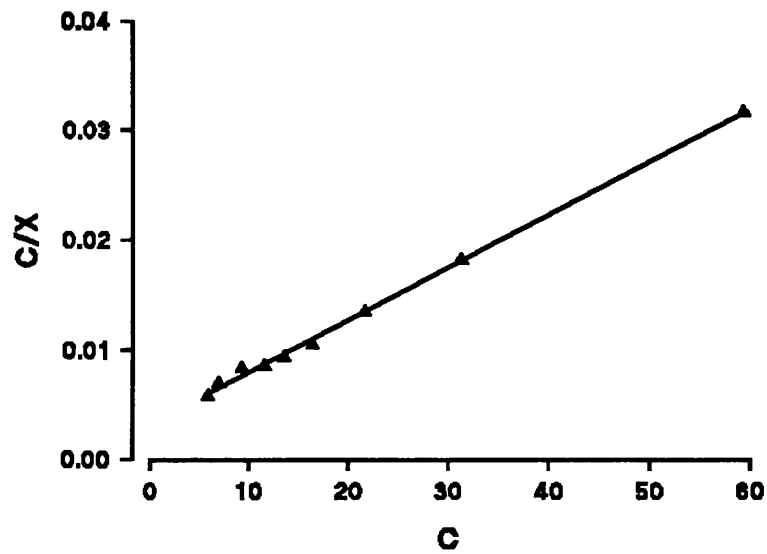


Fig 4.60 Langmuir isotherm for desorption of Zinc in Amlaird soil in $NaNO_3$ background.

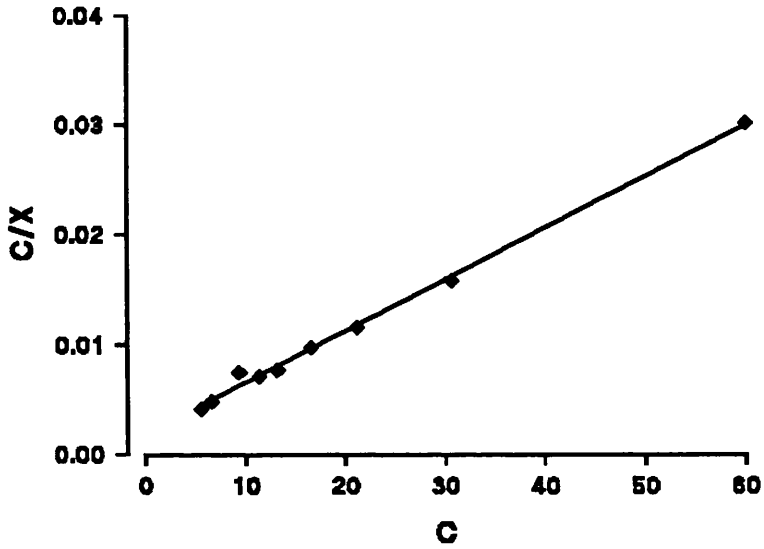


Fig 4.61 Langmuir isotherm for desorption of Zinc in Dunlop soil in $NaNO_3$ background.

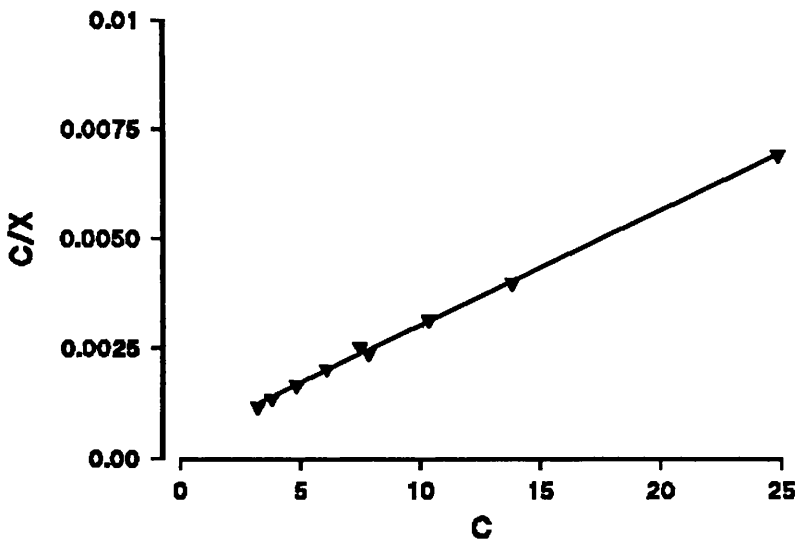


Fig 4.62 Langmuir isotherm for desorption of Zinc in Midelney soil in $NaNO_3$ background.

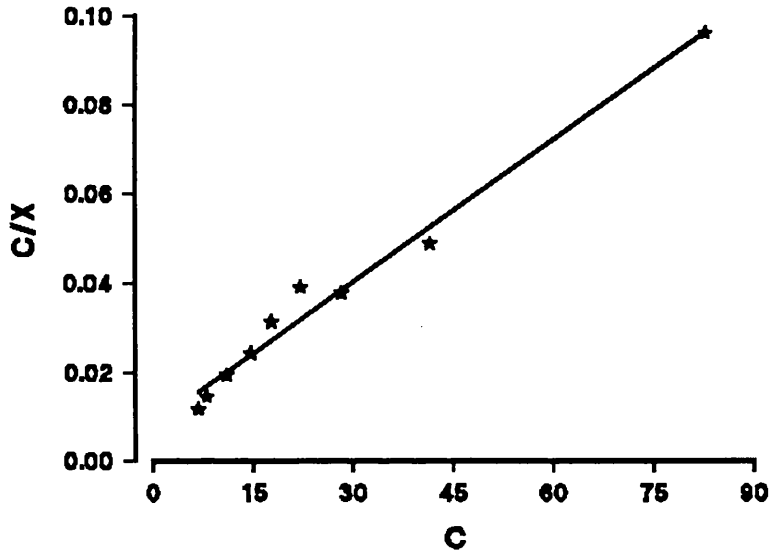


Fig 4.63 Langmuir isotherm for desorption of Zinc in Dreghorn soil in $NaNO_3$ background.

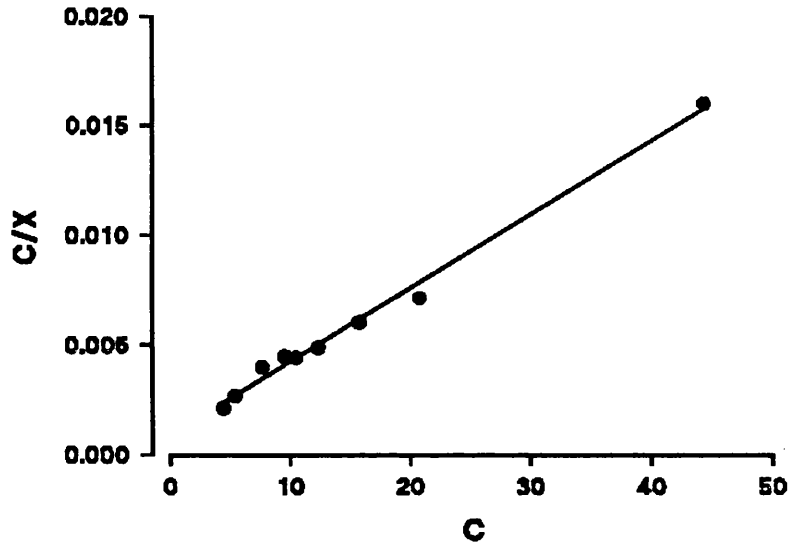


Fig 4.64 Langmuir isotherm for desorption of Copper in Caprington soil in $NaNO_3$ background.

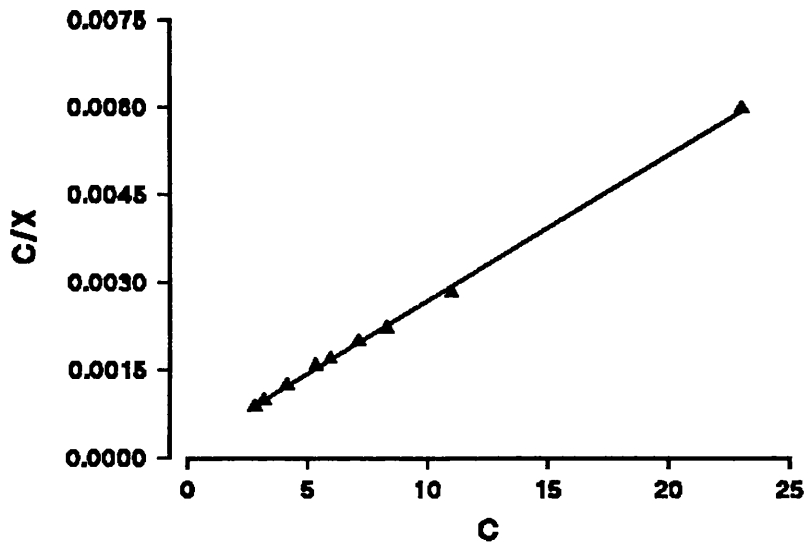


Fig 4.65 Langmuir isotherm for desorption of Copper in Amlaird soil in $NaNO_3$ background.

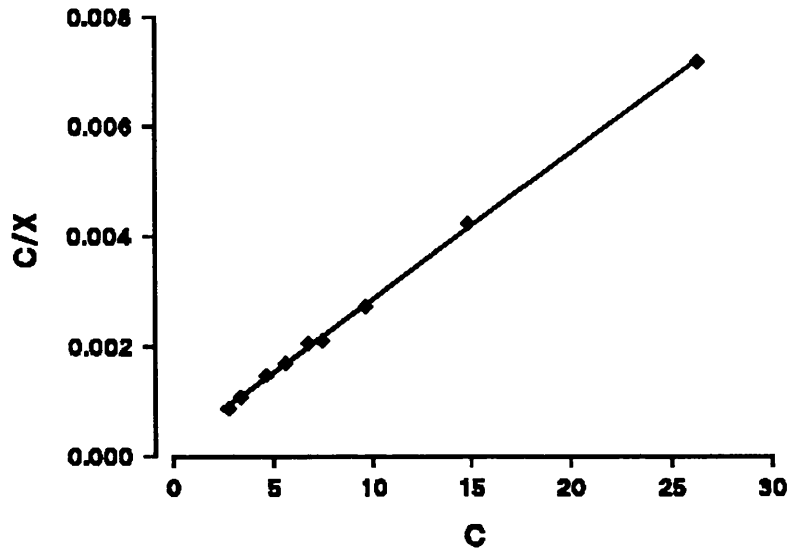


Fig 4.66 Langmuir isotherm for desorption of Copper in Dunlop soil in $NaNO_3$ background.

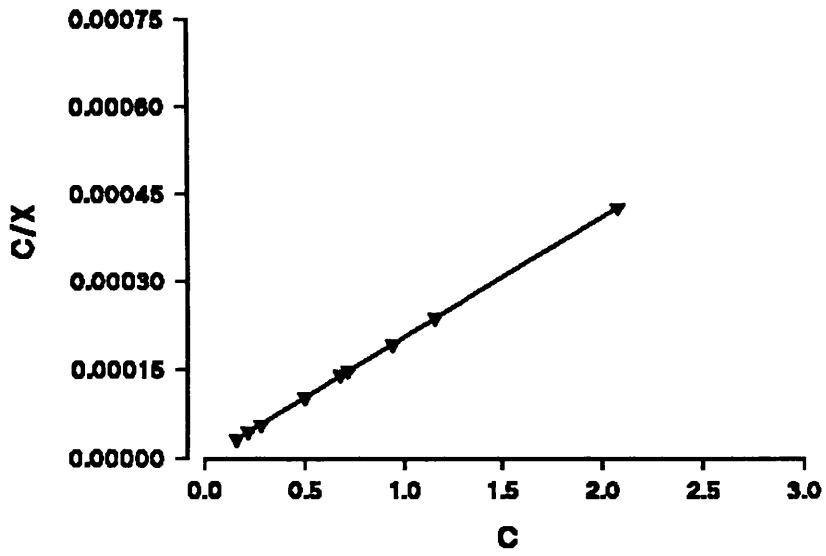


Fig 4.67 Langmuir isotherm for desorption of Copper in Mideiney soil in $NaNO_3$ background.

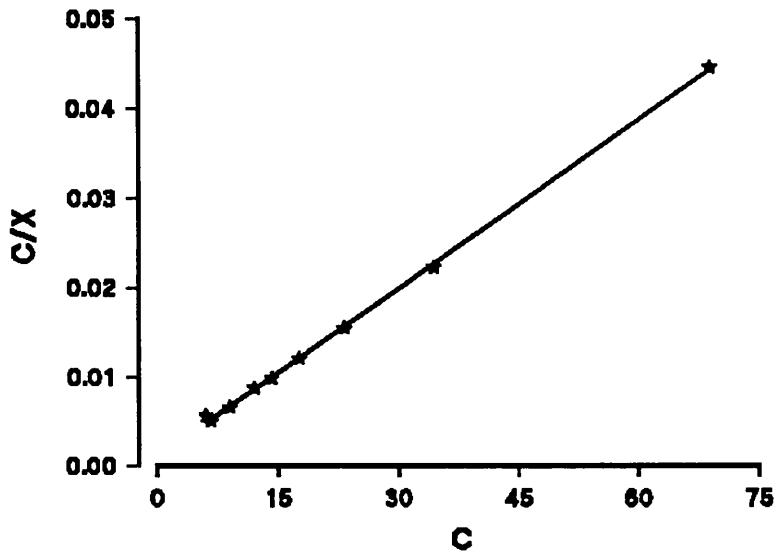


Fig 4.68 Langmuir isotherm for desorption of Copper in Dreghorn soil in $NaNO_3$ background.

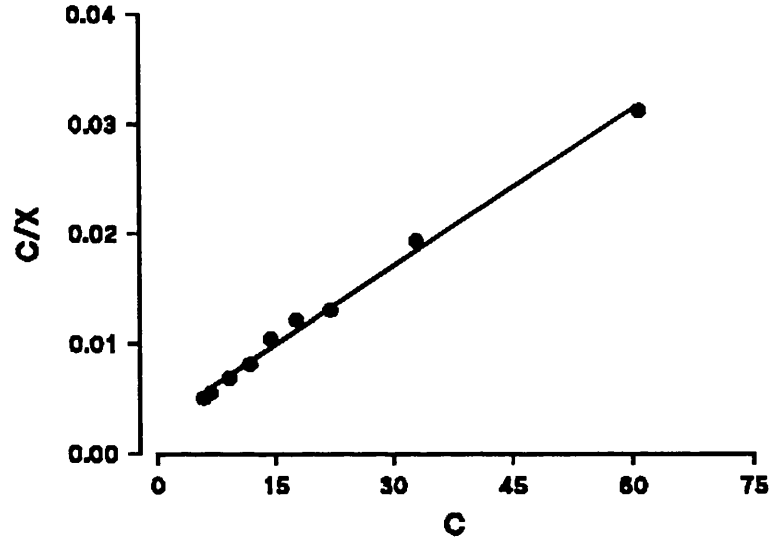


Fig 4.69 Langmuir isotherm for desorption of Nickel in Caprington soil in $NaNO_3$ background.

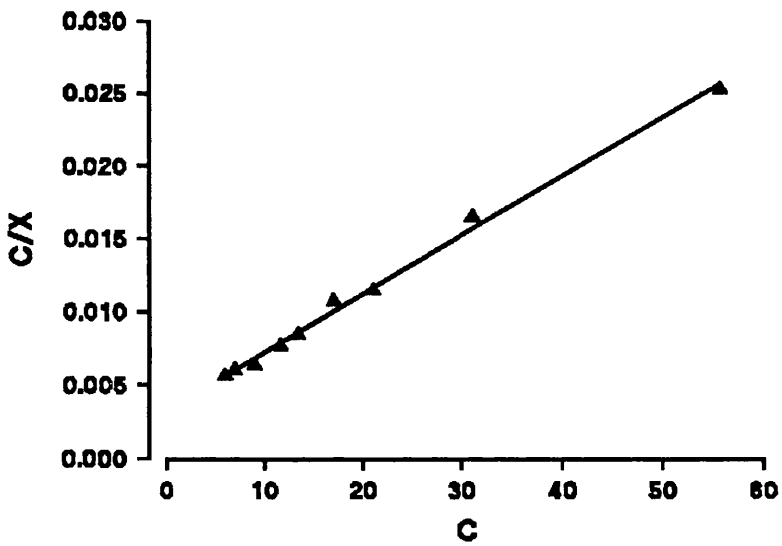


Fig 4.70 Langmuir isotherm for desorption of Nickel in Amlaird soil in $NaNO_3$ background.

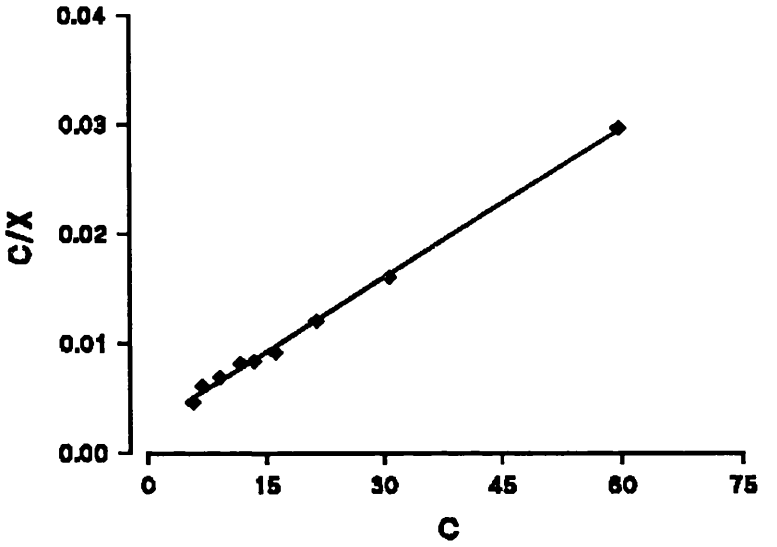


Fig 4.71 Langmuir isotherm for desorption of Nickel in Dunlop soil in $NaNO_3$ background.

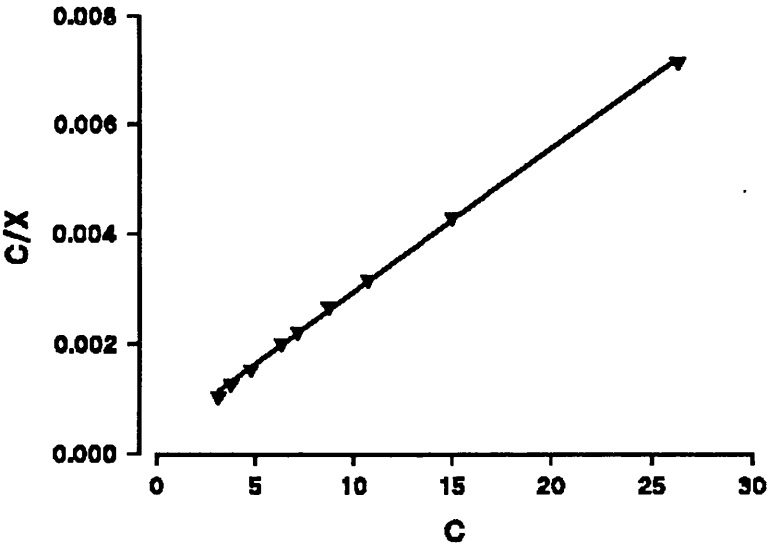


Fig 4.72 Langmuir isotherm for desorption of Nickel in Mideiney soil in $NaNO_3$ background.

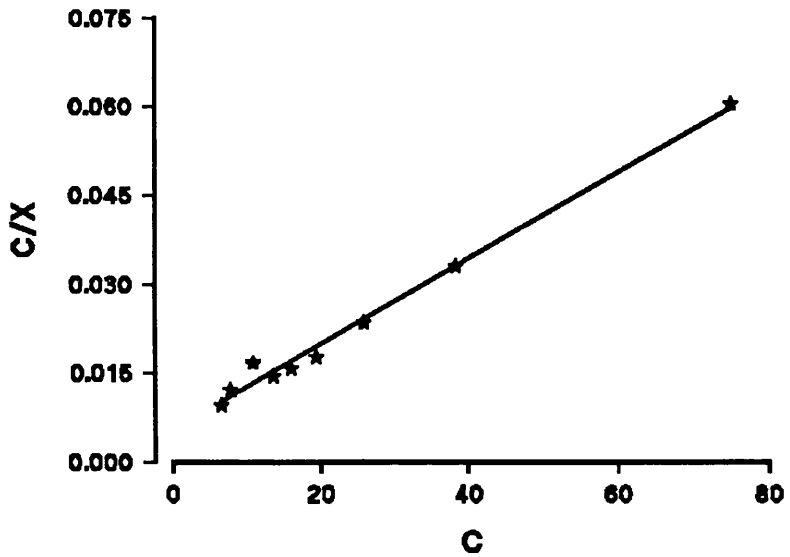


Fig 4.73 Langmuir isotherm for desorption of Nickel in Dreghorn soil in $NaNO_3$ background.

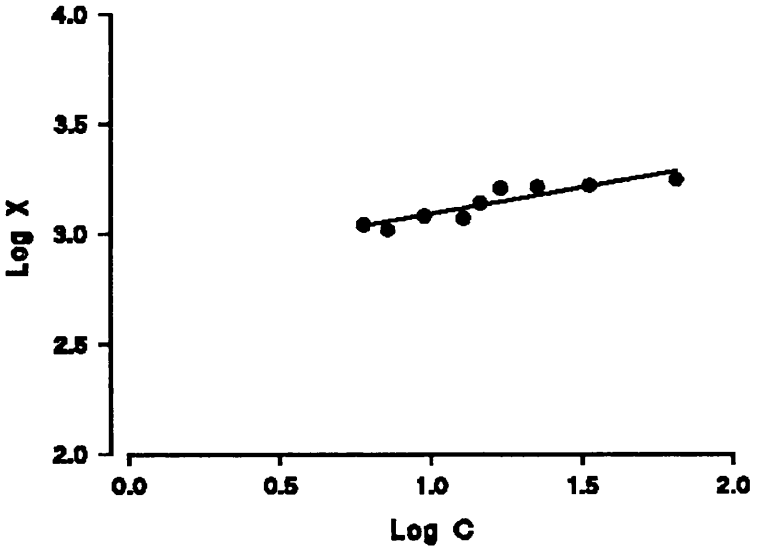


Fig 4.74 Freundlich isotherm for desorption of Zinc in Caprington soil in $NaNO_3$ background.

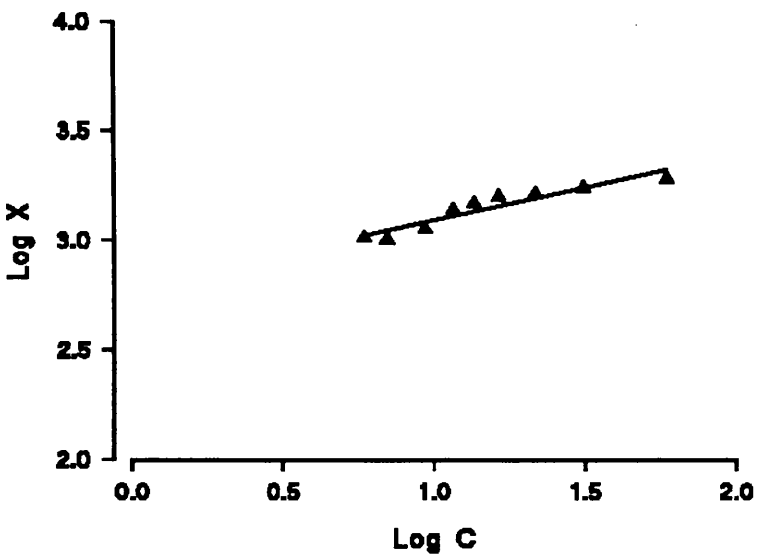


Fig 4.75 Freundlich isotherm for desorption of Zinc in Amlaird soil in $NaNO_3$ background.

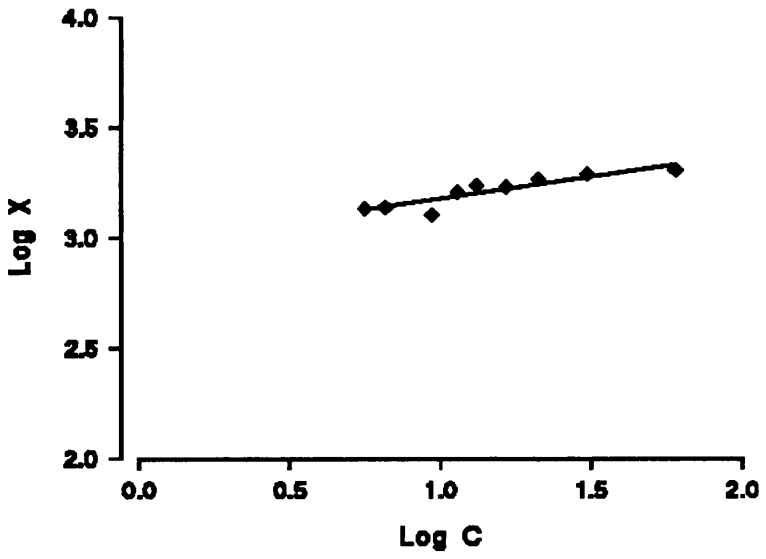


Fig 4.76 Freundlich isotherm for desorption of Zinc in Dunlop soil in $NaNO_3$ background.

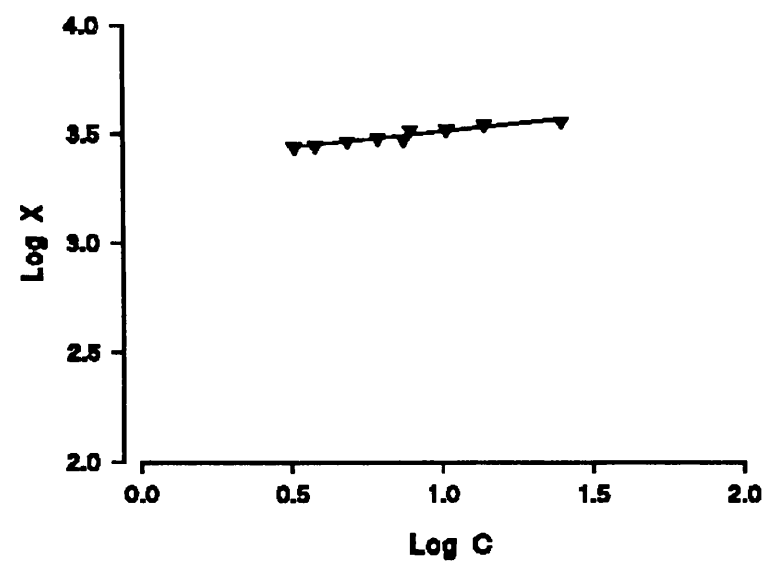


Fig 4.77 Freundlich isotherm for desorption of Zinc in Midelney soil in $NaNO_3$ background.

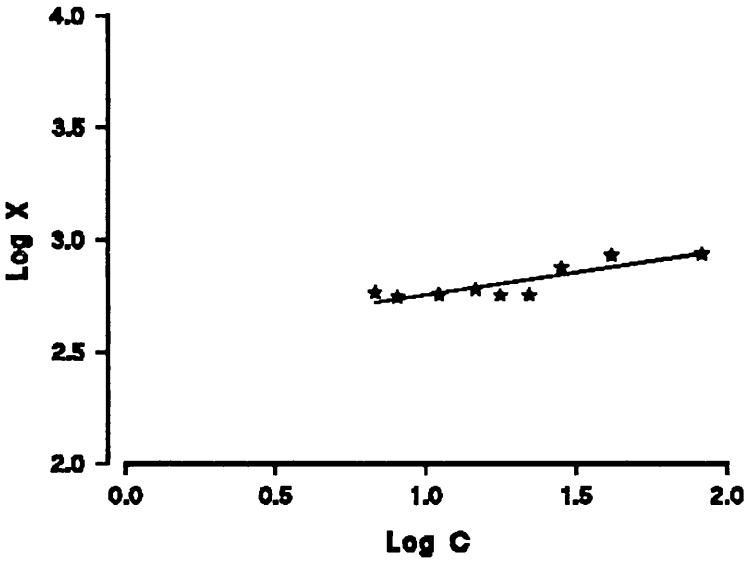


Fig 4.78 Freundlich isotherm for desorption of Zinc in Dreghorn soil in $NaNO_3$ background.

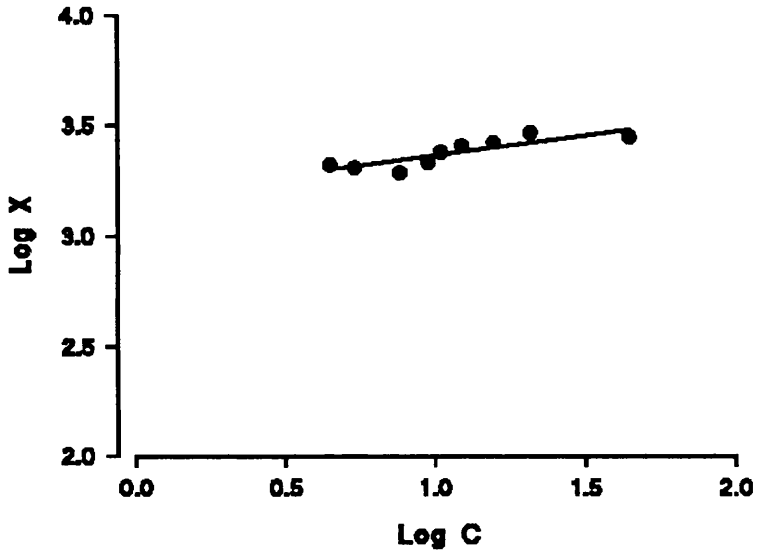


Fig 4.79 Freundlich isotherm for desorption of Copper in Caprington soil in $NaNO_3$ background.

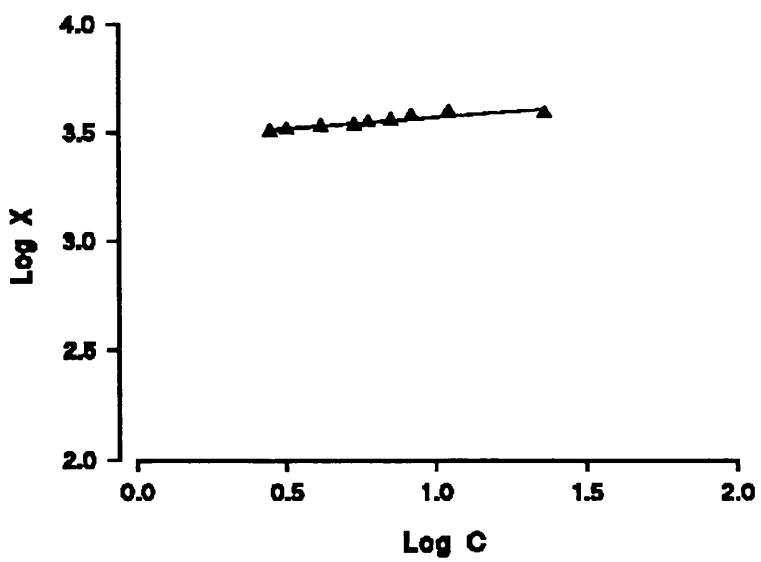


Fig 4.80 Freundlich isotherm for desorption of Copper in Arnlaird soil in $NaNO_3$ background.

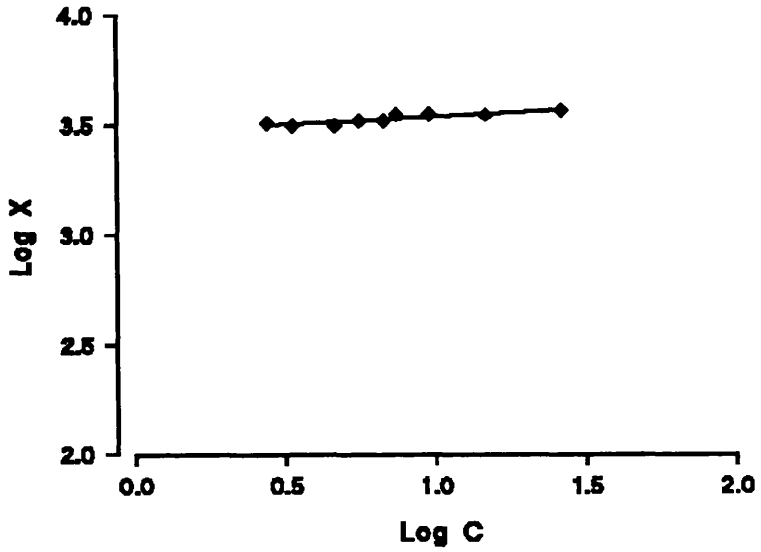


Fig 4.81 Freundlich isotherm for desorption of Copper in Dunlop soil in $NaNO_3$ background.

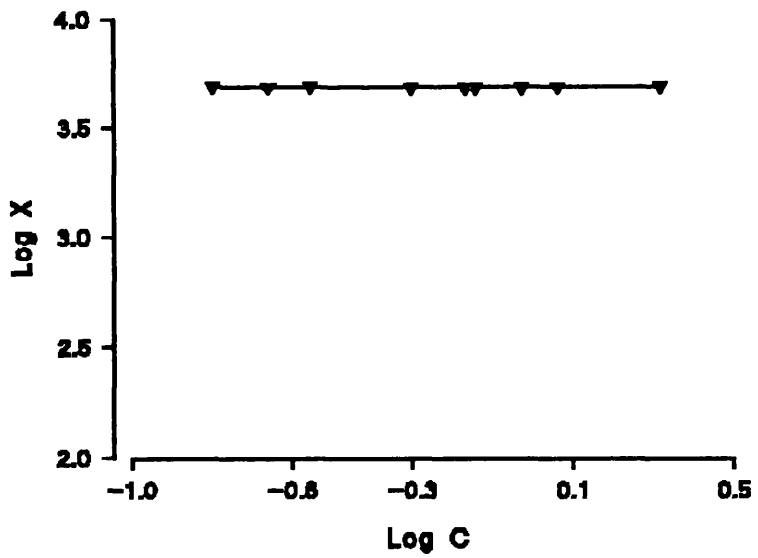


Fig 4.82 Freundlich isotherm for desorption of Copper in Midelney soil in $NaNO_3$ background.

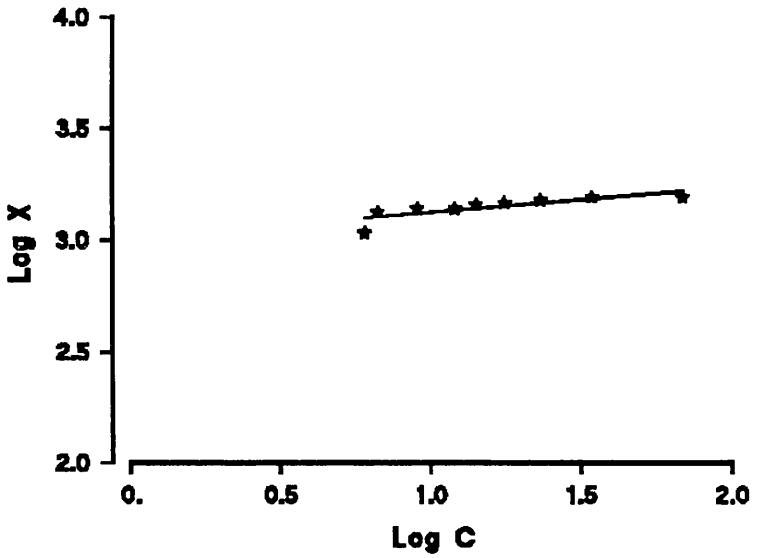


Fig 4.83 Freundlich isotherm for desorption of Copper in Dreghorn soil in $NaNO_3$ background.

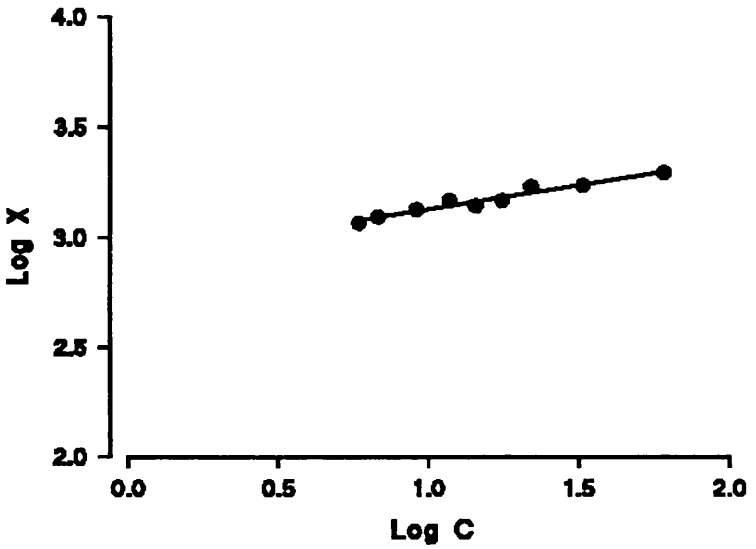


Fig 4.84 Freundlich isotherm for desorption of Nickel in Caprington soil in $NaNO_3$ background.

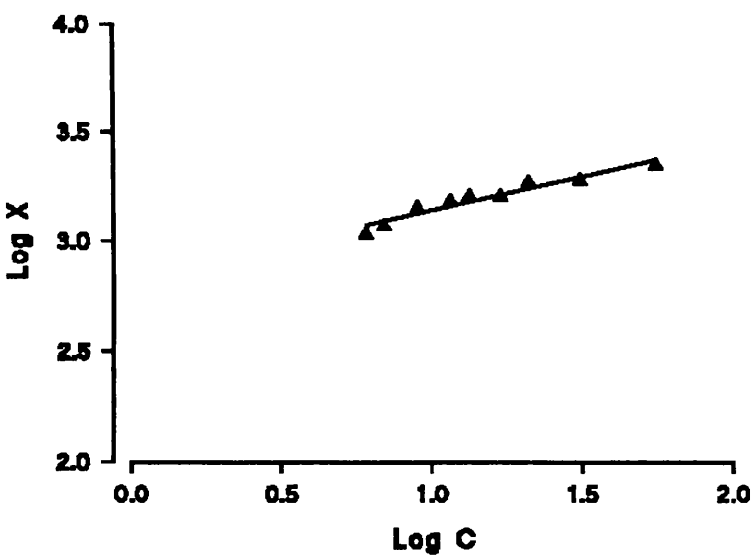


Fig 4.85 Freundlich isotherm for desorption of Nickel in Amlaird soil in $NaNO_3$ background.

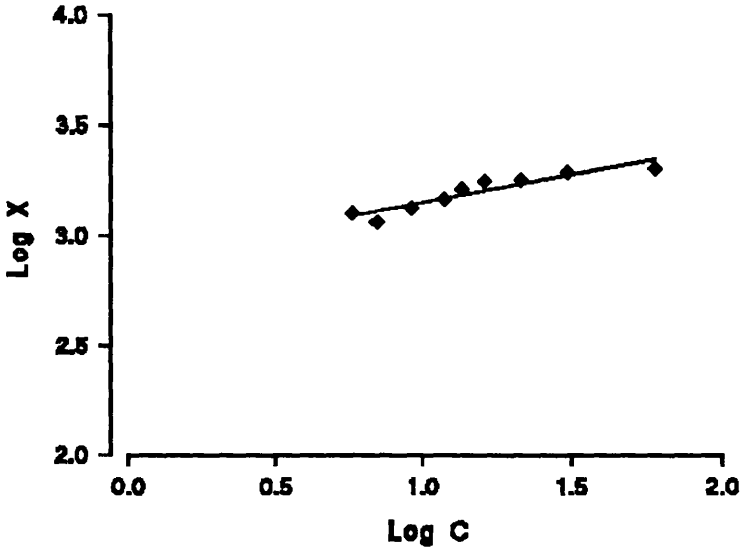


Fig 4.86 Freundlich isotherm for desorption of Nickel in Dunlop soil in $NaNO_3$ background.

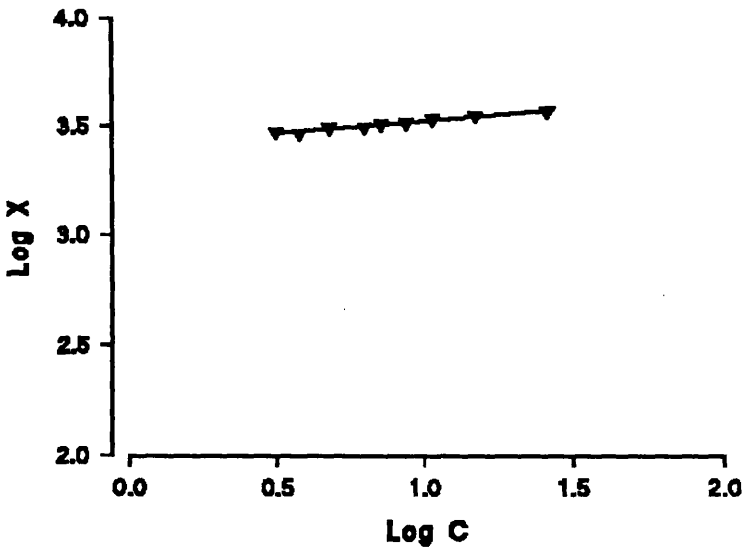


Fig 4.87 Freundlich isotherm for desorption of Nickel in Mideiney soil in $NaNO_3$ background.

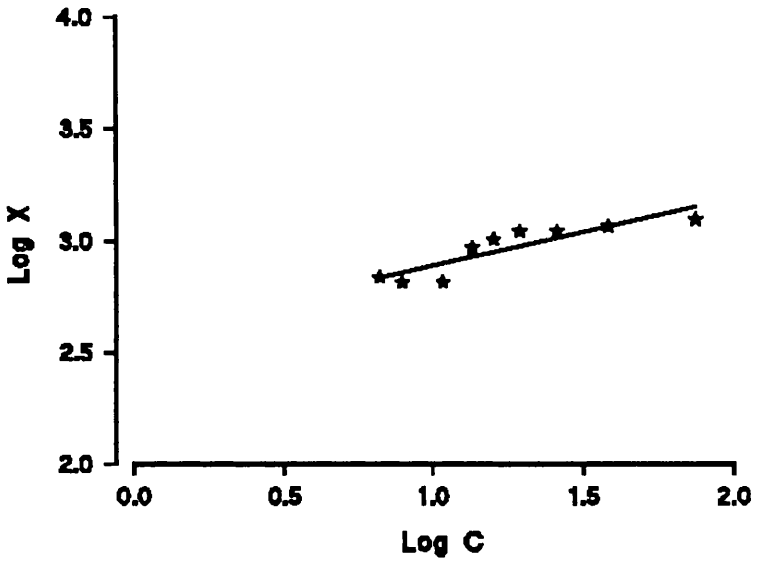


Fig 4.88 Freundlich isotherm for desorption of Nickel in Dreghorn soil in $NaNO_3$ background.

to its linear form, but it did not prove better than Langmuir isotherm and very poor correlation coefficients were obtained. There fore the desorption will further be discussed only according to Langmuir equation and much concentration will be given to this equation as it did show good fit compared to Freundlich equation.

Desorption constants of the five soils for zinc, copper and nickel were calculated from Langmuir as well as Freundlich isotherms and are placed in Tables 4.2, 4.4, 4.6 (see in the pages of adsorption study). The zinc desorption maxima was in order of Dreghorn > Caprington ≥ Amlaird ≥ Dunlop > Midelney and the bonding energy was as Midelney > Dunlop > Caprington > Amlaird > Dreghorn. The desorption maxima for copper and nickel was in similar order in the soils and they revealed the order of desorption maxima as Dreghorn > Caprington > Dunlop > Amlaird > Midelney. The bonding energy sequence of copper was differnt than nickel, and the copper bonding energy order was Midelney > Dunlop ≥ Amlaird > Dreghorn > Caprington. The nickel bonding energy sequence was in order Midelney > Dunlop > Caprington > Amlaird > Dreghorn.

The soils having high clay and relatively greater in pH than others, had the desorption maxima lower for all the three metals in general. Therefore the Midelney soil showed the lowest desorption maxima while the Dreghorn and Caprington soils presented the highest desorption maxima. The former soil (Midelney) is known as clayey (Bakhsh, 1988) and the later two are relatively low in clay contents.There fore it seems that the texture of the soils

have most probably played a role in the adsorption and desorption capacity of the soils for the three metals. All the soils according to Langmuir plot gave a very good correlation co-efficients (R^2) for all the three metals. For zinc it showed the range from 0.980-0.999, the range for copper was 0.991-1.000 and for nickel it was 0.994-0.999, excluding the R^2 for Dreghorn soil i.e. R^2 = 0.889 which does not conform to the Langmuir Isotherm and also to the Freundlich isotherm where it gives R^2 = 0.779.

Freundlich equation did not conform better than Langmuir to the desorption data obtained for zinc, copper, nickel in soils and therefore need not to be discussed further as already data best fit to the Langmuir equation. It is unlikely to express the data by Freundlich isotherm when the data better fit according to Langmuir equation. The preference of Langmuir isotherm over Freundlich isotherm is due to the information it gives about the adsorption and desorption maxima of the soils along with the correlation coefficients, but Freundlich plot only gives us information about slope, intercept and R^2 which could not be considered more important than the informations obtained from Langmuir plot whenever it suits to the data of adsorption or desorption of metals in soils.

Chapter 5

Temperature effect on the adsorption and desorption of zinc in soils

5.1 Introduction

According to Barrow (1986a) temperature may have two distinct effects on a chemical reaction; it may affect the rate of approach to equilibrium and the position or state of the equilibrium. The rate of any chemical reaction increases at high temperatures due to an effective increase in collisions between the molecules. Not only are there more collisions due to high temperature but also the percentage of collisions that have an energy greater than the activation energy also rises.

In general, temperature affects the rate of a reaction because the reaction generates an intermediate, high-energy state and therefore only the molecules with sufficient energy can make the transition over this stage. The higher the temperature, the higher the proportion of the molecules that have sufficient energy and so the faster the reaction. The effect of temperature is therefore best described by the energy required to cross this barrier - the activation energy. The activation energy (Ea) may be defined as the minimum energy required for the reaction to happen. The activation energy is inversely proportional to the rate of the reaction. It means that the lower the activation energy, the faster the reaction; the higher the activation energy, the slower the

reaction will be. Every chemical has different energy levels. In some cases the products are of higher energy than the reactants (''uphill reactions''), but in almost all cases there is an energy hill which has to be overcome-the activation energy. The top of the energy hill is called the transition state and whenever the reacting molecules react this point, one or more original bonds are broken and one or more new bonds formed. The entire system at this point is called the activated complex. An energy diagram for a typical reaction is given in Fig. 5.1.

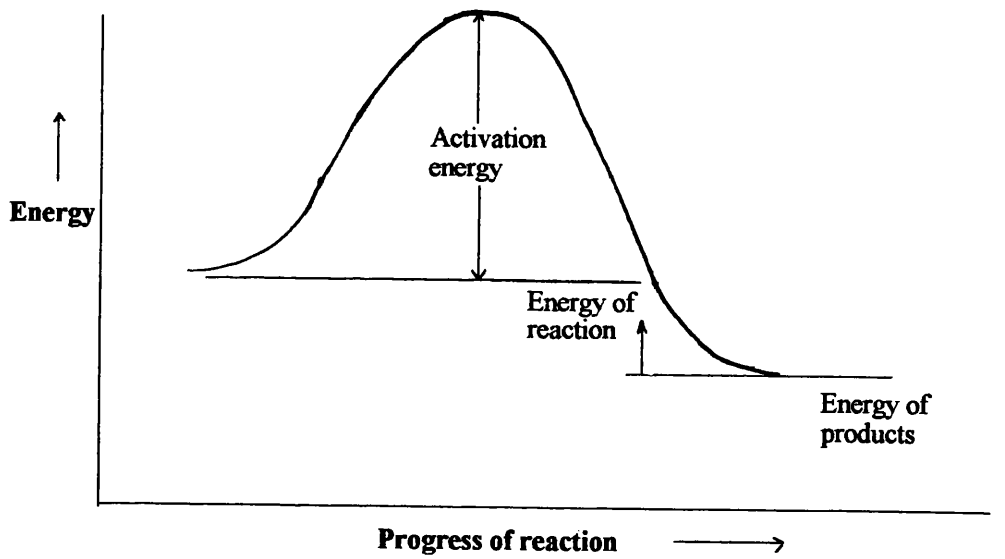


Fig. 5.1 Energy diagram for a typical reaction from Bettelheim and March, 1988.

An optimum temperature should be kept in mind whenever the deficiency of any metal be recovered by applying fertilizers, otherwise the required metal nutrient may not be available to plants effectively. Brennan et al. (1980, 1984) have observed a subsequent decrease in the effectiveness of copper fertilizers at high temperatures. It may either be adsorbed onto soil or precipitated making insoluble or unexchangeable forms due

to temperature variations. Barrow (1986a) stated that increasing the temperature increased the rate of the slow reaction that followed zinc adsorption. It also changed the position of equilibrium of the initial adsorption reaction. He also assumed that an initial, rapid, adsorption reaction was followed by diffusive penetration of the surface. Assaad and Nielsen (1984) found that adsorption of copper increased by decreasing the experimental temperature. The soils they used for the study of copper adsorption were Danish arable soils. Their findings are in contradiction with the results of Barrow (1986). However, in an another paper Assaad and Nielsen (1985) reported that zinc adsorption increased with the increase of temperature, indicating that adsorption is an endothermic process. They used the same soils which were studied for copper adsorption.

Jorda et al. (1992) worked on effect of temperature on the kinetics of Fe EDDHA sorption on a calcareous soil and reported high activation energy between 38.5 and 61.8 kJ/mol and attributed the adsorption process to a non diffusional process. They further claimed that Fe concentration was decreased at higher temperatures. At 323K and 48h of interaction, the quantity of iron in solution was approximately 80% of the initially added Fe, whereas at 333K, it was reduced to 60%. According to their results the sorption of Fe EDDHA was an endothermic, non spontaneous process of high energy, which indicated specific sorption.

Keeping in view the importance of temperature in the study of adsorption/desorption of trace metals the present work was initiated with the aim of having a thermodynamic approach for trace metals adsorption/desorption in some British soils. Zinc was taken as a typical element in this study due to its vital role in agricultural crop production. In the following sections the effect of different temperatures will be seen in respect of this trace metal adsorption and desorption in soils. All the data regarding adsorption/desorption will be discussed with the help of graphs showing the Temperature versus x (amount adsorbed/g of soil) and logx versus 1/T for all soils and the activation energy will be calaulated from the regression of log x versus 1/T from the Arrhenius equation;

log k= constant + slope 1/T or

k= A exp (-Ea/RT) and

slope= -Ea/2.303xR

where 'Ea' is activation energy in kJ/mol, R is the gas constant in kcal/mol, T denotes absolute temperature and A is a constant.

5.2 Effect of temperature on the adsorption of zinc in soils

This study consists of all the five soils already studied in the previous chapters for adsorption of zinc at room temperature. It is an obvious fact that fluctuation of soil temperature influences the availability of plant nutrients including micronutrients. Thus it was decided to

conduct an experiment under controlled conditions to study how the different temperatures affect the adsorption of zinc in soil and the possible mechanisms controlling its adsorption in soil.

5.2.1 Method

Four different temperatures (5°C, 10°C, 20°C and 25°C) were selected, and each treatment was allocated three replicates, before initiating the experiment. Then one g of each soil (< 2 mm) was taken in four ounce glass bottles and pre-equilibrated with 25 cm^3 of 0.1 M $NaNO_3$ solution at controlled temperatures in an orbital shaker for 1.5 hours. The shaker was set at 180 r.p.m. After pre-equilibration of the sodium nitrate-soil suspension, 25 cm^3 from one of the stock solutions (60, 180 and 200 μg Zn cm^{-3}) were added and the shaker was run for 18 hours at a set temperature. The samples were filtered through Whatman filter No.1 and measured by atomic absorption spectrophotometry. Activation energy was calculated by applying the data to the Arrhenius equation. Further details about the procedure can be seen in Chapter 2 Section 2.7.

5.2.2 Results and discussion

The effects of temperature on the adsorption of zinc by soils have been represented in figures 5.2-5.6, simply by plotting the amount of zinc adsorbed in $\mu g\ g^{-1}$ of soil versus different temperatures. All the soils gave a positive response to the increase of temperature in

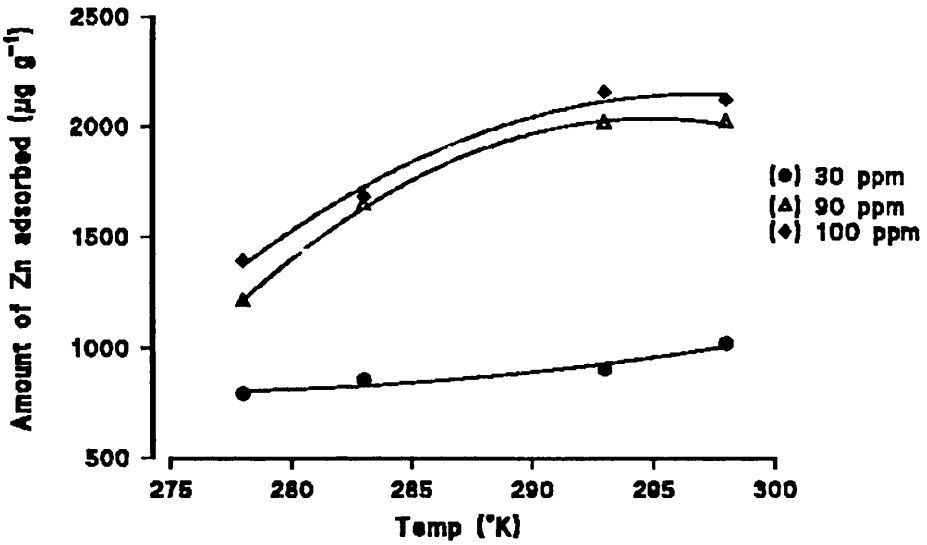


Fig. 5.2 Temperature effect on the adsorption of Zinc in Caprington soil.

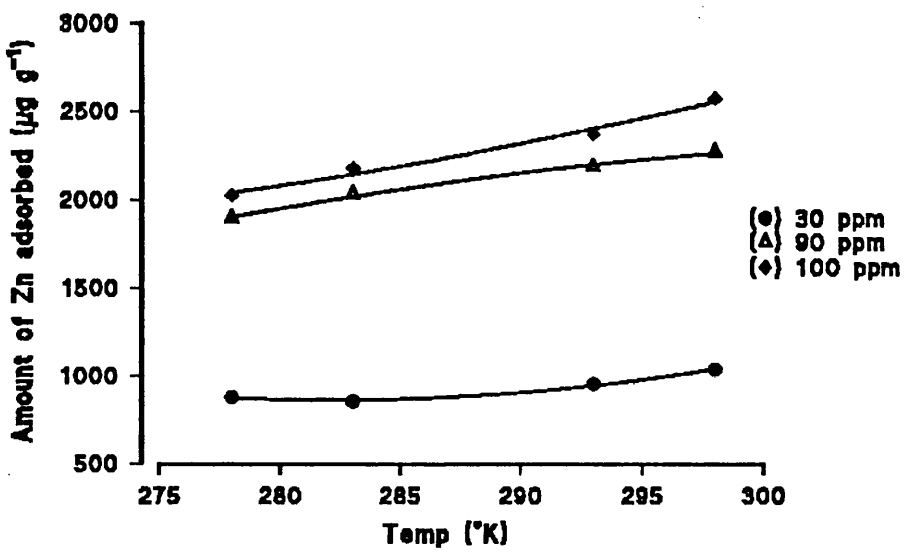


Fig. 5.3 Temperature effect on the adsorption of Zinc in Amlaird soil.

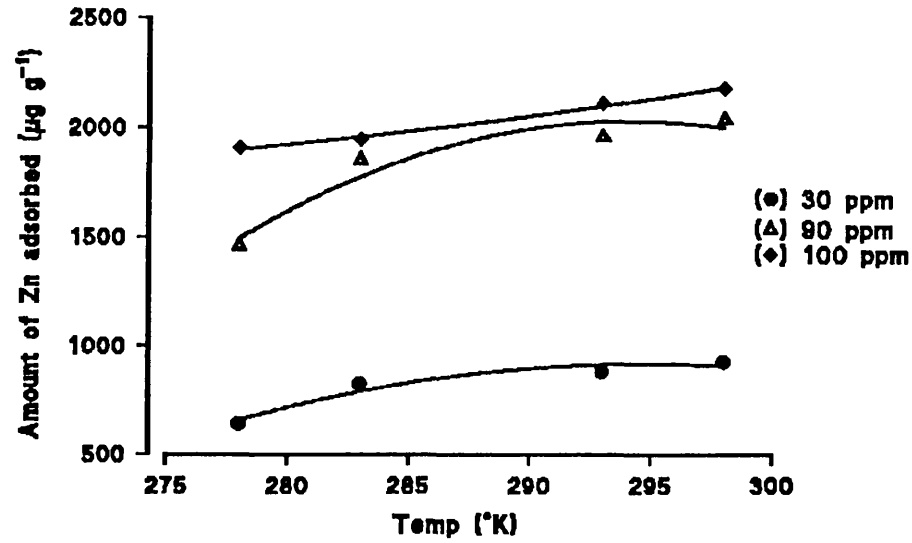


Fig. 5.4 Temperature effect on the adsorption of Zinc in Dunlop soil.

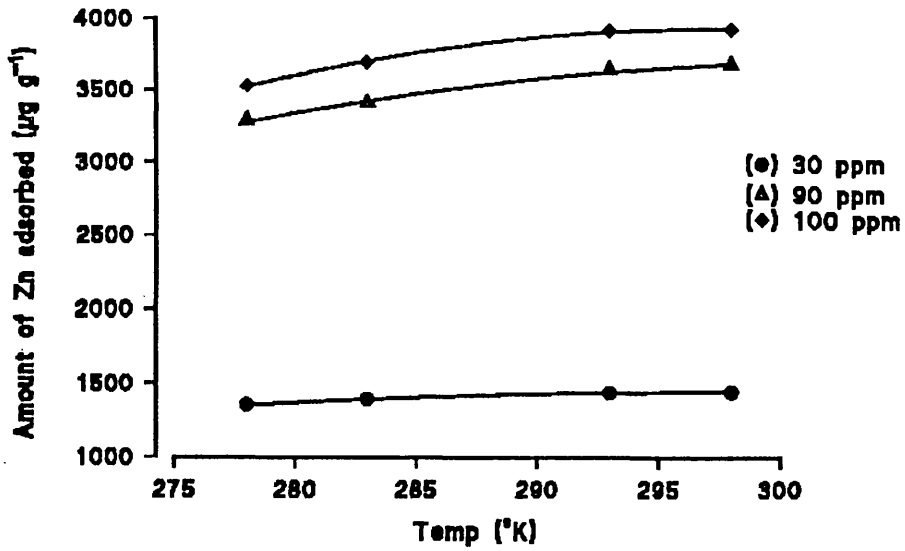


Fig. 5.5 Temperature effect on the adsorption of Zinc in Mideiney soil.

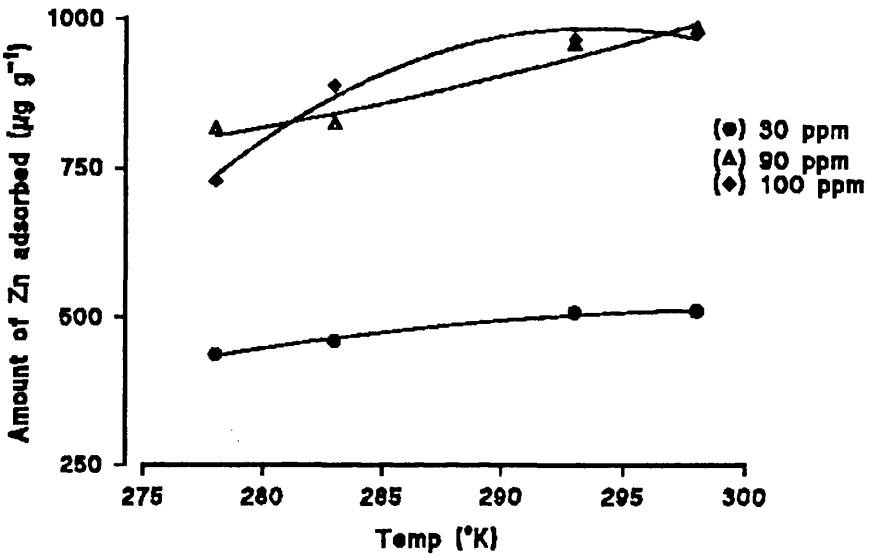


Fig. 5.6 Temperature effect on the adsorption of Zinc in Dreghorn soil.

respect of zinc adsorption. Some soils showed little response while others had more significant response in adsorption of zinc with respect to temperature increase. These findings are well supported by the findings of Assaad and Nielsen (1985) and Barrow (1986). Barrow (1992) suggested that in most cases an increase in temperature increased the sorption of cations-an effect compatible with the effects of temperature on both the rate of reaction and the position of an adsorption equilibrium involving cations. Relan et al. (1980) have shown that adsorption maxima were increased with the increasing of temperature. They observed adsorption maxima of 8.33, 11.11, and 12.00 ($\mu g\ g^{-1}$) at temperatures 22°C, 28°C and 38°C respectively.

Table 5.1 shows the effect of temperature on the adsorption of zinc by the five soils from the three initial concentrations of zinc used. It is evident from the table that, with the exception of Dunlop soil, comparatively more zinc was adsorbed from the higher concentrations at higher temperatures. Moreover, it shows that with increasing temperature adsorption of zinc is also increased.

For all the soils log x (adsorbed amount of zinc) versus 1/T (temperature) has been plotted (figs. 5.7-5.11) and activation energy and R^2 to show the goodness of fit of a straight line to the data were calculated (Table 5.2). For all the soils and concentration treatments straight lines have been drawn. Amlaird and Midelney soils

TABLE 5.1 Maximum percent increase of zinc adsorption on soils due to temperature increase in soil-Zn solution system.

Soil		Amount of zinc adsorbed in $\mu g\ g^{-1}$ at specified temperature				
		5°C	10°C	20°C	25°C	Maximum % increase
Caprington	30ppm	792	854	902	1021	30
	90ppm	1208	1644	2010	2015	67
	100ppm	1392	1684	2153	2119	53*
Amlaird	30ppm	876	852	950	1033	18
	90ppm	1895	2030	2184	2267	20
	100ppm	2024	2176	2366	2566	27
Dunlop	30ppm	639	823	876	924	45
	90ppm	1457	1848	1954	2035	40
	100ppm	1906	1945	2111	2179	14
Midelney	30ppm	1351	1392	1434	1439	7
	90ppm	3281	3405	3631	3664	12
	100ppm	3524	3690	3907	3914	11
Dreghorn	30ppm	437	460	507	510	17
	90ppm	813	821	953	980	21
	100ppm	728	887	963	973	34

Note: Each value is a mean of three.
* = Mean calculated from the underlined figures.

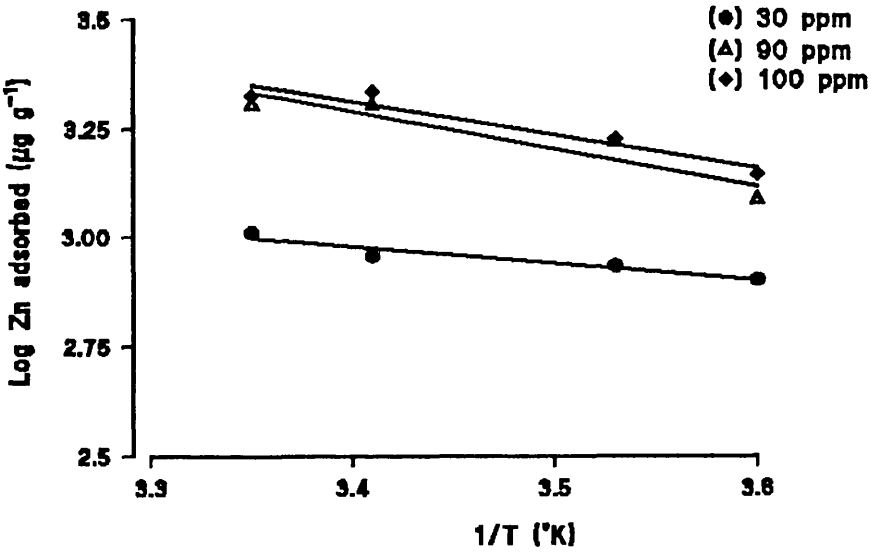


Fig. 5.7 Arrhenius plots for Zinc adsorption by Caprington soil.

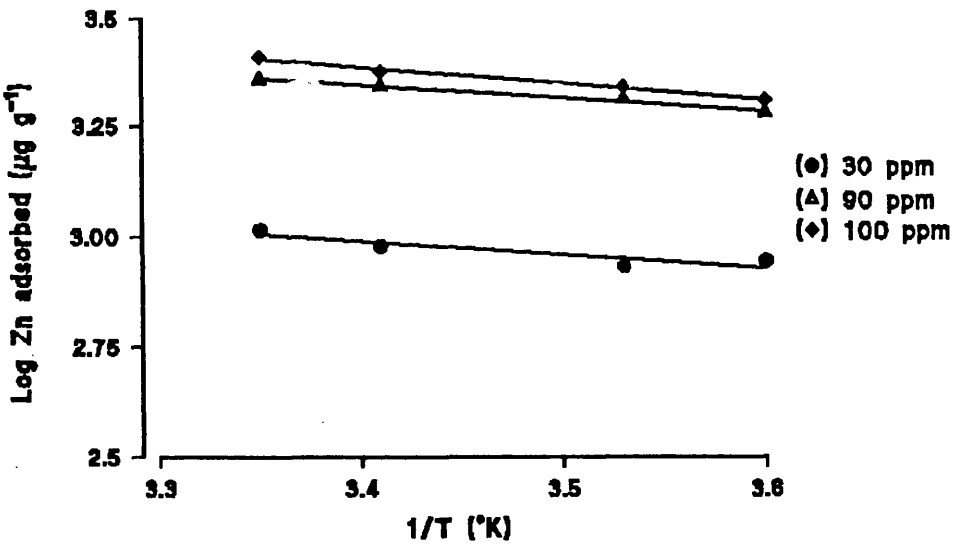


Fig. 5.8 Arrhenius plots for Zinc adsorption by Amlaird soil.

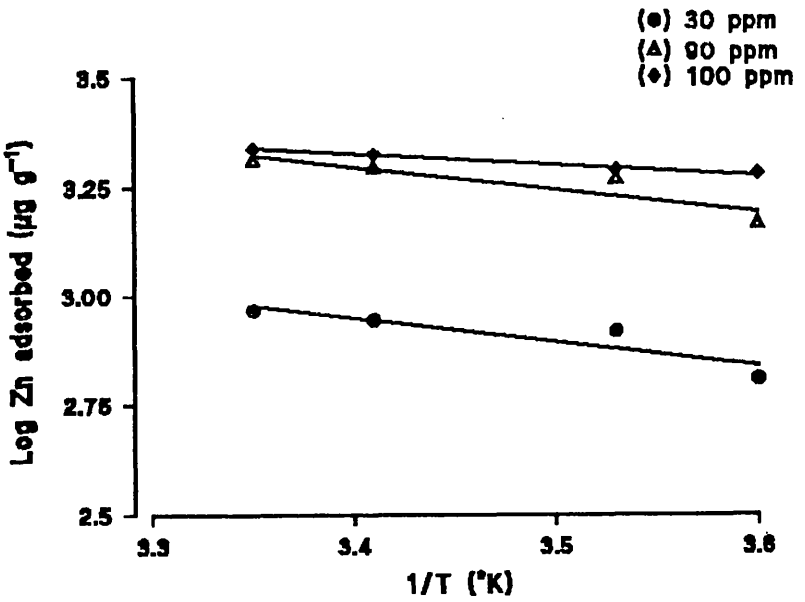


Fig. 5.9 Arrhenius plots for Zinc adsorption by Dunlop soil.

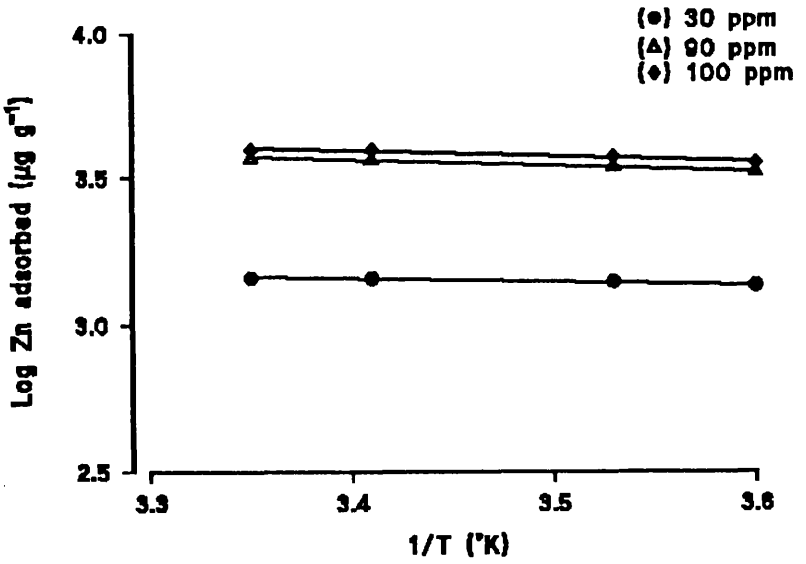


Fig. 5.10 Arrhenius plots for Zinc adsorption by Mideiney soil.

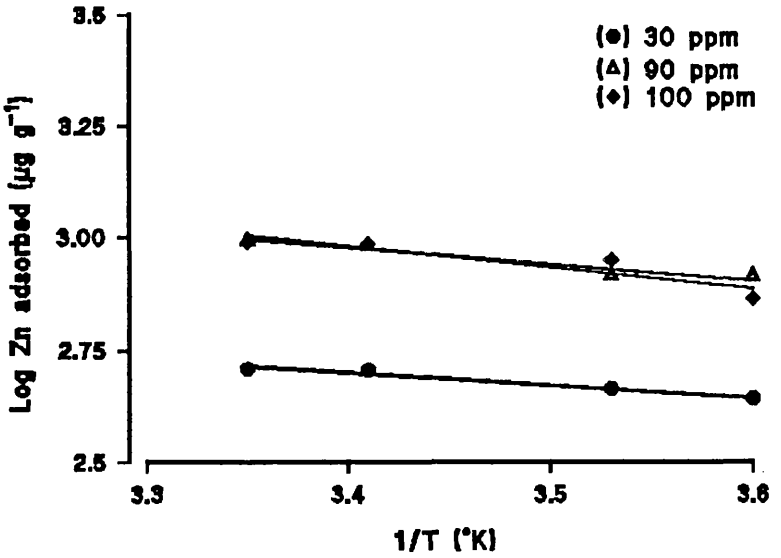


Fig. 5.11 Arrhenius plots for Zinc adsorption by Dreghorn soil.

TABLE 5.2 Activation energy (Ea) for adsorption of zinc on different soils and goodness of fit of a straight line (R^2).

Soil		Activation energy (Ea) KJ/mole	R^2 %
Caprington	30pmm	7.54	92
	90pmm	16.60	88
	100pmm	14.65	93
Amlaird	30pmm	5.80	83
	90pmm	5.88	99
	100pmm	7.49	99
Dunlop	30pmm	10.88	82
	90pmm	9.86	81
	100pmm	4.67	98
Midelney	30pmm	2.11	95
	90pmm	3.83	98
	100pmm	3.60	95
Dreghorn	30pmm	5.46	97
	90pmm	6.97	94
	100pmm	9.02	83

showed good straight lines, It is obvious that activation energy increases with zinc concentration in every soil except Dunlop. The reason may be that it becomes increasingly difficult for zinc ions to be adsorbed on to a surface as the adsorbing sites fill up and the surface becomes covered. It is also clear from the Table 5.2 that activation energy for the adsorption of zinc is the highest in Caprington, while Midelney shows the lowest activation energy for all concentration treatments. It is also evident from the same Table 5.2 that the values of activation enegy are low, therefore it suggests that the factor controlling zinc adsorption is diffusion. Furthermore it suggests that this adsorption process is endothermic also as, with the increase of temperature adsorption of zinc was increased. Similar reports were given by Kuo and Mikkelsen 1979 and Assaad and Neilsen 1985.

5.3 Effect of temperature on the desorption of zinc in soils.

By desorption we simply mean the bringing back of the adsorbed element into solution. We can assume that adsorption is achieved by increasing the metal ion concentration, while the reversibility of the adsorption reaction is induced in response to a reduction of the solution concentration of the metal. Generally, by this way, very little desorption of heavy metals occurs (McLaren et al; 1986), but it is unclear whether the

surface reaction is genuinely irreversible or simply very slow in the reverse direction.

Studies of Pb^{2+} adsorption and desorption by goethite suspension have indicated that the adsorption reaction step is fast and probably diffusion controlled ($K_1 \approx 2x10^5$ $mol^{-1}dm^3s^{-1}$), whereas the desorption is much slower ($K_{-1} \approx 6x10^2$ $mol^{-1}dm^3s^{-1}$), probably limited by the activation energy required to break the Pb^{2+} surface bond (Hayes and Leckie, 1986). Adamson (1976) stated that adsorption may or may not require a significant activation energy, but desorption always requires a significant activation energy, since desorption necessitates that the energy of adsorption be overcome. Earlier Barrow (1979), Chien et al. (1982), and Sheppard and Racz (1984) have shown that high temperatures during the desorption phase also increase the rate of the reaction.

In this study of desorption the same five soils studied previously for adsorption at four different temperatures, have been investigated to estimate the effect of temperature on the desorption of zinc from soils. The calculated data have been expressed by graphs, tables and thermodynamic parameters especially in terms of activation energy as before.

5.3.1 Method

0.2 g of each soil was pre-equilibrated with 5 cm^3 of 0.1M $NaNO_3$ for 1.5 hours in the same orbital shaker, used for adsorption at different fixed temperatures. Then 5 cm^3 of 200 μg cm^{-3} zinc solution in form of $ZnSO_4$ was

added to the samples of each treatment, having 3 replicates each. The soil-zinc suspension was then allowed to equilibrate for 18 hours shaking at 180 r.p.m. After attaining equilibrium in the solution, the samples were diluted by 0 times, 2 times and 6 times with 0.1M $NaNO_3$ solution. Each dilution was done within the orbital shaker to avoid the effect of room temperature on the adsorption or desorption of zinc in soils. The samples after 18 hours more shaking for desorption were quickly filtered through Whatman filter No.1, and analysed by atomic absorption spectrophotometry. For more detail of the method and calculation Chapter 2 Section 2.8 can be referred.

5.3.2 Results and Discussion

Temperature versus the amount of zinc adsorbed in $\mu g\ g^{-1}$ of soil from the treatments (0T, 2T, and 6T dilution) is represented in figures 5.12-5.16. Each figure has 3 curves in accordance with the three different dilution points. All the figures show that dilution has an effect on the desorption of zinc in all the soils. The highest dilution of 6 times shows greater amount of zinc desorption than other dilutons in all the soils. Null dilution points of the desorption curves are almost same as adsorption isotherm points from the highest concentration (100 μg Zn cm^{-3}) for each temperature treatment and for each soil. A small difference could be due to the extra time of contact, otherwise no significant difference is evident. For more comprehension help can be taken from the tables 5.1 and 5.3 as adsorption and

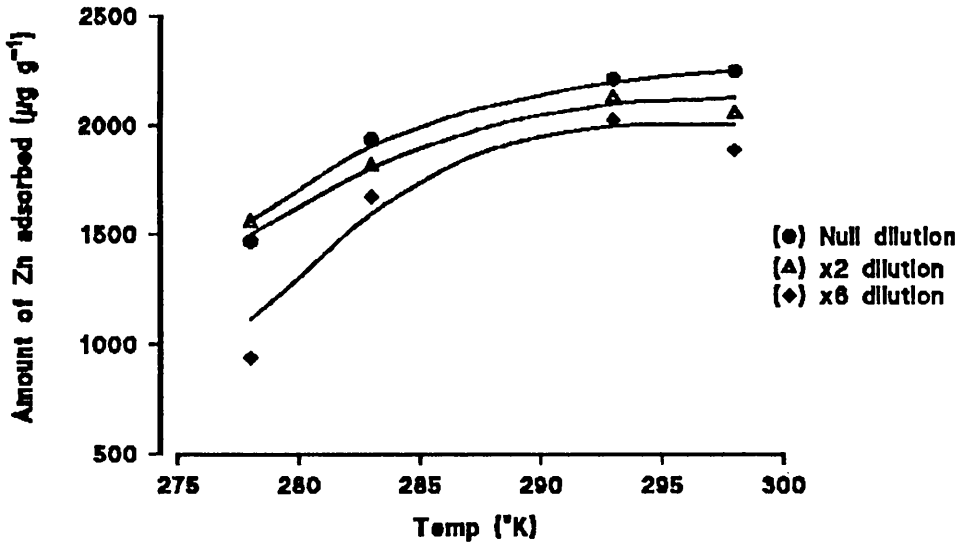


Fig. 5.12 Effect of temperature on the desorption of Zinc in Caprington soil after differential dilutions.

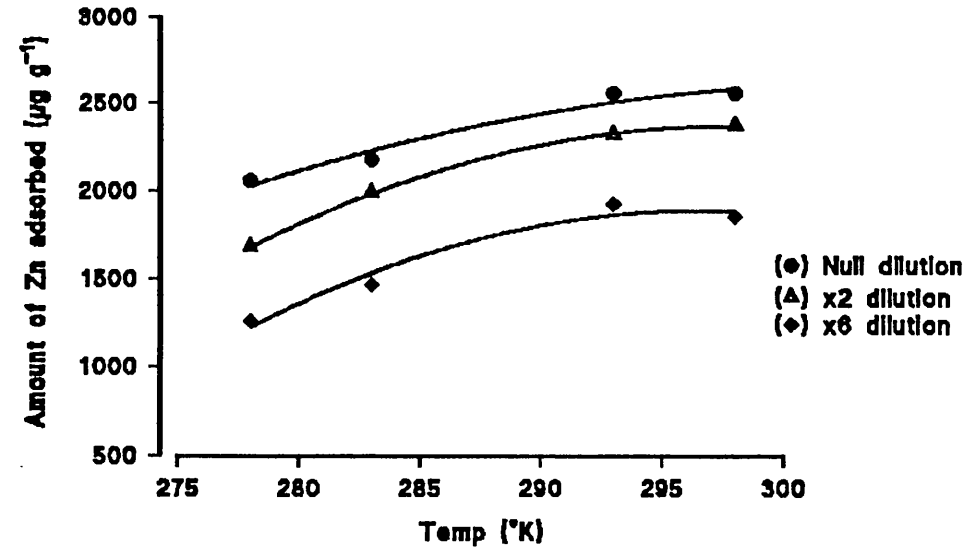


Fig. 5.13 Effect of temperature on the desorption of Zinc in Amlaird soil after differential dilutions.

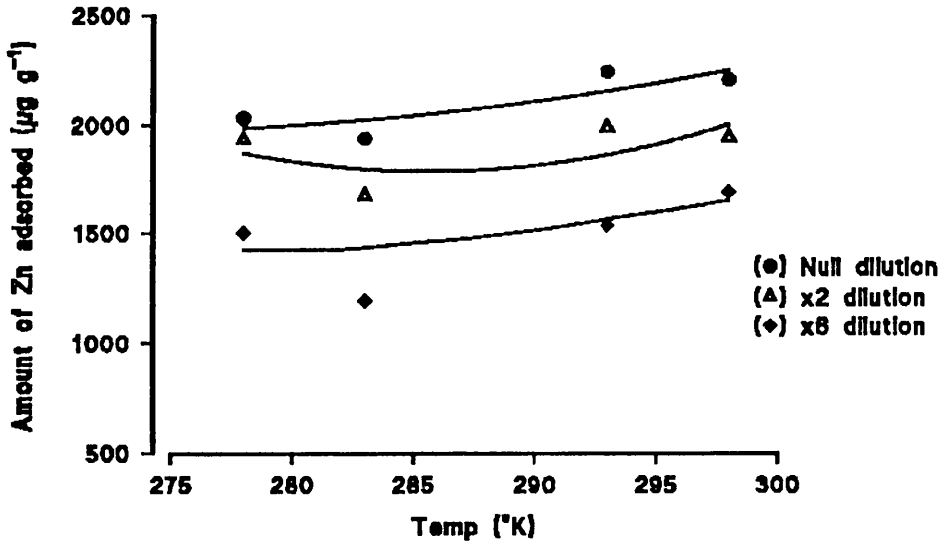


Fig. 5.14 Effect of temperature on the desorption of Zinc in Dunlop soil after differential dilutions.

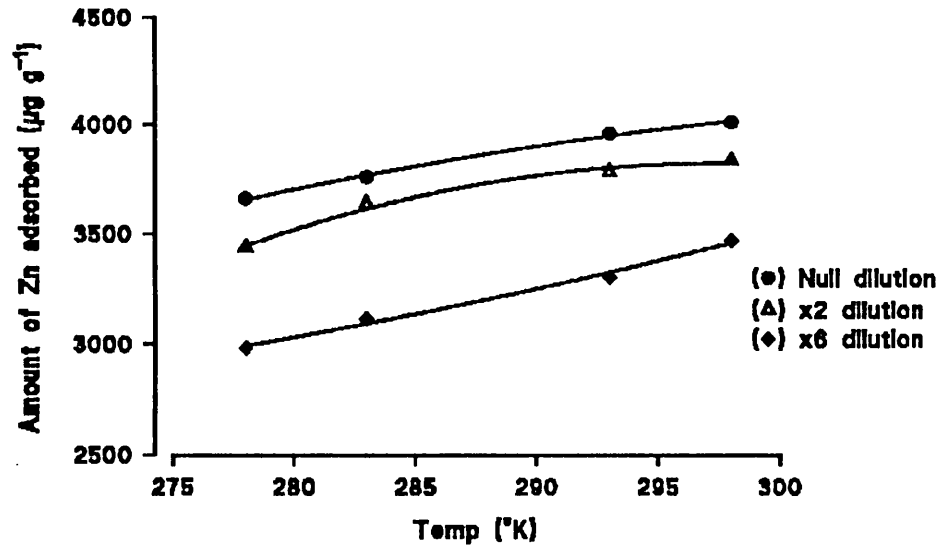


Fig. 5.15 Effect of temperature on the desorption of Zinc in Midelney soil after differential dilutions.

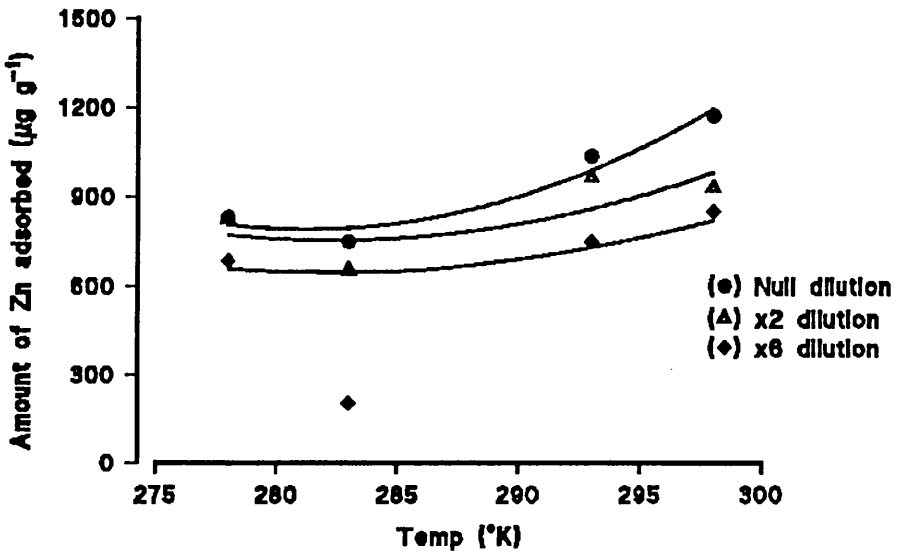


Fig. 5.16 Effect of temperature on the desorption of Zinc in Dreghorn soil after differential dilutions.

TABLE 5.3 Amount of zinc adsorbed per gram of soil from 10 cm^3 of a 100 μg cm^{-3} solution following differential dilution of 0, 2 and 6 times, at four temperatures. Figures in paranthesis denote the % desorption at each dilution. The right hand column shows the maximum % increase in adsorption due to temperature.

Soil	Dilution (Times)	Temperature(°C) 5°C	10°C	20°C	25°C	Maximum % increase
Caprington	0	1468	1935	2215	2252	53 %
	2	1552	1810	2127	2053	
		(0)	(6)	(4)	(9)	–
	6	938	1670	2024	1886	–
		(36)	(14)	(9)	(16)	–
Amlaird	0	2054	2175	2550	2550	24 %
	2	1677	1987	2317	2367	
		(18)	(9)	(9)	(7)	–
	6	1256	1466	1925	1850	–
		(39)	(32)	(24)	(27)	–
Dunlop	0	2030	1937	2240	2205	10 %
	2	1932	1672	1987	1940	
		(5)	(14)	(13)	(12)	–
	6	1502	1193	1535	1691	–
		(26)	(38)	(31)	(23)	–
Mideleney	0	3660	3757	3954	4005	9 %
	2	3435	3632	3780	3830	
		(6)	(3)	(5)	(4)	–
	6	2981	3113	3302	3467	–
		(19)	(17)	(17)	(13)	–
Dreghorn	0	828	749	1033	1170	41 %
	2	823	650	962	928	
		(0.6)	(13)	(7)	(9)	–
	6	683	203	749	848	–
		(18)	(73)	(27)	(27)	–

Note :The figures in paranthesis denote the % desorption with respect to dilution times.

desorption isotherms have not shown in one graph. The temperature effect on the desorption of zinc followed the same pattern observed for adsorption. In general the desorption of zinc decreased with the increase of temperature, but at 25°C further decrease in the desorption is either seemed to finish or biased towards no significant reduction in desorption in most of the soils in diluted treatments. At high temperatures no further decrease in the desorption of zinc in most soils may be due to a phenomenon stated by Barrow (1987) that high temperatures increase desorption, because increasing the temperature decreases the value of binding constant. He further elaborated that a higher concentration of the adsorbing material is required in solution in order to maintain the same amount of adsortion, however these effects may be modified by the effects of temperature. Assaad and Nielsen (1984) also found an increase in the desorption of copper at higher temperature.

Dunlop and Dreghorn soils show a desorption of zinc at 10°C with all dilution treatments (figures 5.14, and 5.16 respectivey) but then they follow the same trend of a decrease in desorption of zinc as the other soils, with respect to increase of temperature. This strange behaviour of both the soils at 10°C could not be explained.

The effect of temperature on the desorption of zinc has been also shown in Table 5.3. The effect of dilution on the desorption of zinc in terms of percentage can be seen in the vertical columns, while the effect of temperature on the desorption of zinc can be seen in the

horizontal lines. It is obvious from the vertical columns that zinc is desorbed more and more when there is more and more dilution of the soil-zinc system, but it is decreased when temperature is increased (horizontal lines). Dunlop and Dreghorn soil unusually indicate some increase in the desorption at 10°C, however it carries after this point the behaviour of low desorption like other soils. 6 times dilution gave more desorption of zinc compared to 2 times dilution in all the soils. The maximum adsorption percentage from no dilution treatment in the desorption study (Table 5.4) is almost equal to the maximum percentage of adsorption of zinc from the highest concentration in the adsorption study (Table 5.1), in all the soils.

Figures 5.17-5.21 represent 1/T (temperature) versus log x (adsorbed zinc) for all soils. Each figure is consist of three curves allocated for 0T, 2T and 6T dilution with 0.1M $NaNO_3$ solution. Amlaird, Dunlop and Midelney soils produced very good straight lines when the data was plotted according to Arrhenius equation. The other two soils (Caprington and Dreghorn) produced better straight lines and well fit to the Arrhenius equation when one very apart point from other points in each soil was neglected.

The thermodynamic parameters obtained by plotting 1/T versus log x have been placed in the Table 5.4. The soils which responded positively and significantly towards desorption of zinc with respect to joint effects of temperature variation and dilution, gave good correlation

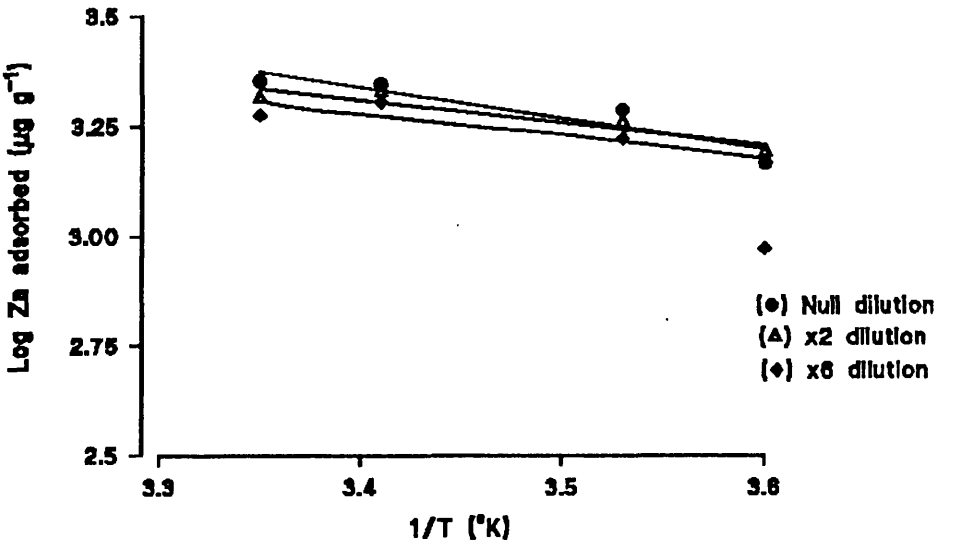


Fig. 5.17 Arrhenius plots for Zinc desorption by Caprington soil after differential dilutions

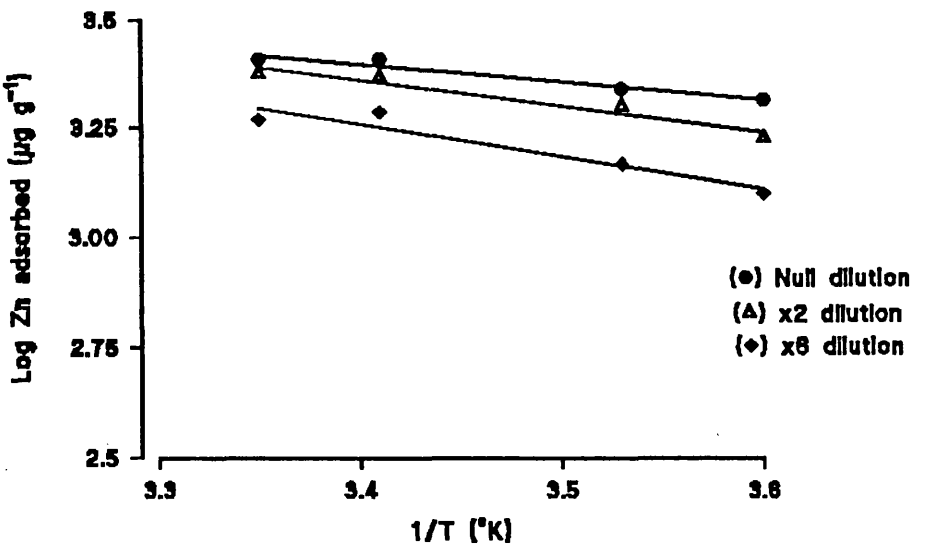


Fig. 5.18 Arrhenius plots for Zinc desorption by Amlaird soil after differential dilutions.

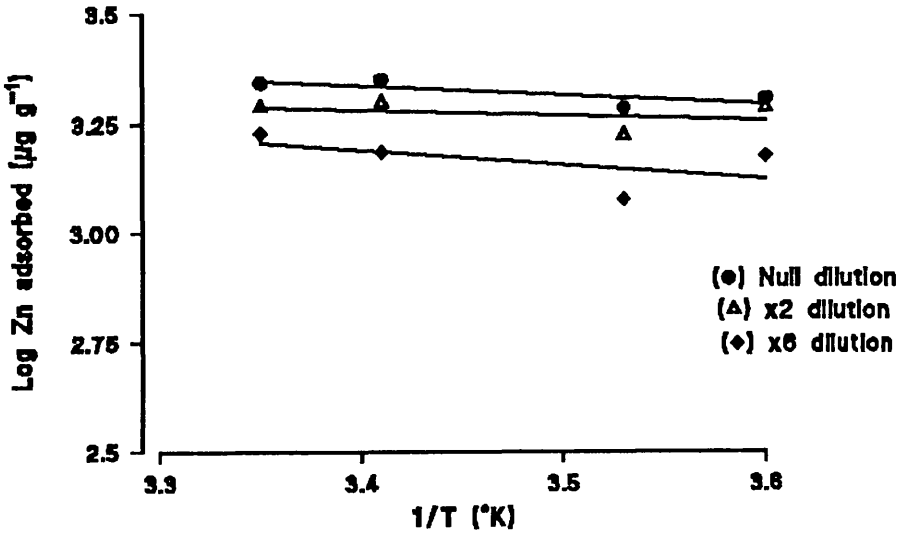


Fig. 5.19 Arrhenius plots for Zinc desorption by Dunlop soil after differential dilutions.

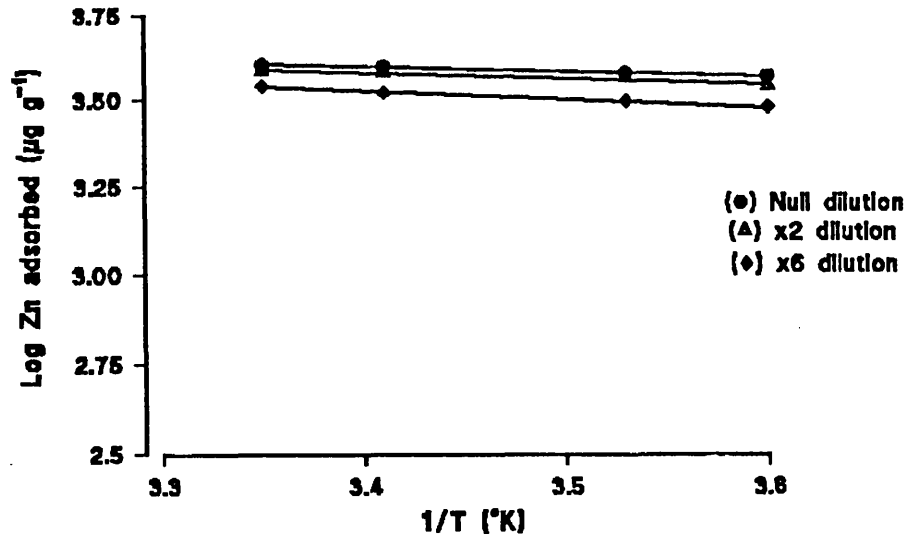


Fig. 5.20 Arrhenius plots for Zinc desorption by Midelney soil after differential dilutions.

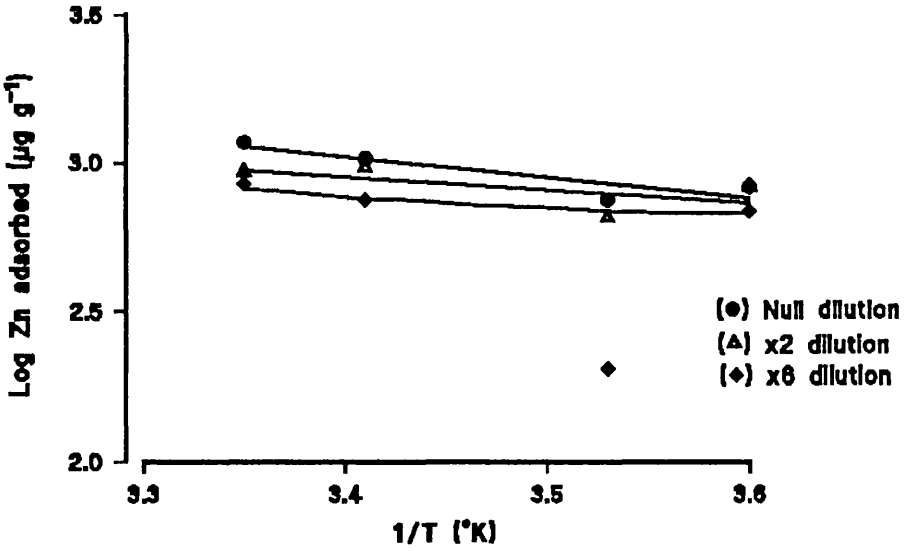


Fig. 5.21 Arrhenius plots for Zinc desorption by Dreghorn soil after differential dilutions.

coefficients as are obvious in Amlaird and Midelney soils. The best R^2 was noted in Midelney and also the least slope in the same soil. The activation energy increased when the dilution was increased to each soil-zinc suspension. This is because of need to break the bonds of adsorption. Amlaird and Midelney soils behaved in similar manner and they showed an increase in the activation energy with the increase of dilution. The other three soils behaved somewhat differently than former two soils, but similar to each other. They showed activation energy at null dilution point higher than two times dilution. Then they gave higher activation energy when dilutions were increased up to 6 times. The increase in activation energy at null dilution points in these soils compared to 2 times dilution may be due to the effect of more contact of soils with zinc solution without driving force of more $NaNO_3$ solution as a dilutor of the zinc concentration in the system. It is well observed fact prolong contact of metal solution with soil increases the adsorption of metal. Barrow (1986a) revealed that with increasing time and temperature, the concentration of zinc in solution is decreased. The increase in activation energy due to dilution increase is generally due to the fact that desorption or reverse reactions always require a significant activation energy to necessitate the energy of adsorption to overcome and to break the adsorption bonds and make some new bonds. However it is not necessary for adsorption reactions to require significant activation energy (Adamson, 1976).

TABLE 5.4 Thermodynamic parameters for desorption of zinc in different soils.

Soil	Dilution (Times)	Activation energy (Ea) (KJ/mole)	R^2 %
Caprington	No dilution	14.00	87
	2T	10.19	87
	6T	22.78	73
Amlaird	0T	8.25	96
	2T	11.81	95
	6T	14.69	93
Dunlop	0T	4.25	83
	2T	2.35	81
	6T	6.38	98
Midelney	0T	3.22	100
	2T	3.62	95
	6T	4.98	97
Dreghorn	0T	13.75	79
	2T	8.50	40
	6T	22.40	20

Comparing the activation energy noted from the highest concentration in these five soils in the adsorption study (Table 5.2), with the activation energy derived from the same concentration with null dilution in the desorption study (Table 5.4),in two independent experiments we can find reasonably good agreement, except, perhaps, for Dreghorn soil. It can be concluded that activation energy did not change during the sorption reactions. The slight variations in the quantity could be due to time lag.

From the whole discussion it can be concluded that increasing the temperature increases the adsorption of zinc and decreases the desorption. Adsorption may or may not require a significant activation energy but desorption always require a significant activation energy, because to break the old bonds and to make some new bonds between the reactants. The low values of activation energy show that diffusion was the controlling factor in all the reactions.

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